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ASPECTS OF THE STATISTICAL MECHANICS OF SIMPLE FLUIDS AND ELECTROLYTES*

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ABSTRACT

This review consists of two main parts. The first part is basically of a pedagogical nature. It deals with the problem of intermolecular forces in liquids and the integral equation formalism as well as the corresponding perturbation theory. The second part deals mainly with the theoretical application to electrolytes, molecular fluids and, most of all, to electrified interfaces or double layer problems. Recent results are presented on the validity of the Gouy-Chapman theory and on anomalous ion adsortion.

RESUMEN

Este artículo de revisión consta de dos partes, la primera es una presentación de carácter pedagógico en la cual se trata el problema de las fuerzas intermoleculares en líquidos y los formalismos de ecuaciones integrales y de teoría de perturbaciones. La segunda parte se refiere a aplicaciones recientes de dichos formalismos en electrolitos y fluidos moleculares y en especial en interfases electrificadas o problemas de doble capa, tales como la validez de la teoría de Gouy-Chapman y la adsorción anómala de iones.

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1. INTRODUCTION

These lectures consist of seven parts

- intermolecular forces
- formalism-integral equations
- formalism-perturbation theory
- application to simple fluids
- application to electrolytes
- application to molecular fluids
- application to electrified interfaces (the double layer)

The core of these lectures is the last three parts. As a result we give only general references in the first four parts and give detailed references only in the last three parts.

2. INTERMOLECULAR FORCES

The basic facts about intermolecular forces are simple. The existence of condensed phases implies that the intermolecular forces are attractive at large distances and the fact that matter does not collapse implies that intermolecular forces are repulsive at short distances.

In principle, we can learn about intermolecular forces by solving Schrödinger's equation for a collection of molecules. Unfortunately, this is not practical. However, we can still learn a lot from quantum mechanics.

The Born-Oppenheimer approximation tells us that we need only solve the electronic problem for a set of static nuclei obtaining a potential energy function, U_N, which depends only on the positions $\underset{\sim}{r}_i$ and orientations Ω_i of the molecules. Thus,

$$U_N = U_N(\underset{\sim}{r}_1,\Omega_1,\cdots,\underset{\sim}{r}_N,\Omega_N). \tag{2.1}$$

Further, we may divide U_N into pair, triplet,$\cdots$terms. Thus,

$$U_N = \sum_{i<j} u(\underset{\sim}{r}_i,\Omega_i,\underset{\sim}{r}_j,\Omega_j) + \sum_{i<j<k} w(\underset{\sim}{r}_i,\Omega_i,\underset{\sim}{r}_j,\Omega_j,\underset{\sim}{r}_k,\Omega_k) + \cdots. \tag{2.2}$$

First consider the pair interaction. We can give some insight by considering a one-dimensional model of a pair of interacting molecules. Let us assume that the electrons in one molecule form an instantaneous dipole (even though the molecule has no dipole moment). This induces a dipole in the second molecule. For simplicity, we consider only one electron on each molecule.

The harmonic resorting force on the electrons is

$$V_h = \frac{1}{2} f(x_1^2 + x_2^2) \quad , \tag{2.3}$$

and the electrostatic force is

$$V_e = e^2 \left[\frac{1}{r} + \frac{1}{r + x_2 - x_1} - \frac{1}{r - x_1} - \frac{1}{r - x_2} \right] . \tag{2.4}$$

Using $r \gg x_1$ and x_2 and expanding

$$V_e = - \frac{2e^2 x_1 x_2}{r^3} + \cdots . \tag{2.5}$$

Schrödinger's equation is thus

$$\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_2^2} + \frac{8\pi\mu}{h^2} \left[E - \frac{1}{2} f x_1^2 - \frac{1}{2} f x_2^2 + \frac{2e x_1 x_2}{r^3} \right] \psi = 0 \quad . \tag{2.6}$$

The variables can be separated by changing variables

$$z_1 = \frac{1}{\sqrt{2}} (x_1 + x_2) \quad , \tag{2.7}$$

$$z_2 = \frac{1}{\sqrt{2}}(x_1 - x_2) \ . \qquad (2.8)$$

Thus

$$\frac{\partial^2\psi_i}{\partial z_i^2} + \frac{8\pi\mu^2}{h^2}\left[E - \tfrac{1}{2} f_i z_i^2\right]\psi_i = 0 \ , \qquad (2.9)$$

where

$$\psi = \psi_1(z_1)\psi_2(z_2) \ , \qquad (2.10)$$

$$f_1 = f - \frac{2e^2}{r^3} \ , \qquad (2.11)$$

$$f_2 = f + \frac{2e^2}{r^3} \ . \qquad (2.12)$$

This is the harmonic oscillator equation. Thus

$$E_i = (n_i + \tfrac{1}{2})\, h\nu_i \ , \qquad (2.13)$$

$$\nu_i = \frac{1}{2\pi}\sqrt{\frac{f_i}{\mu}} \ . \qquad (2.14)$$

The ground state is $E_0 = \frac{1}{2} h(\nu_1 + \nu_2)$. Thus,

$$E_0 = \frac{1}{2} h\nu_0 \left\{\left(1 - \frac{2e^2}{fr^3}\right)^{\frac{1}{2}} + \left(1 + \frac{2e^2}{fr^3}\right)^{\frac{1}{2}}\right\}$$

$$= \frac{1}{2} h\nu_0 + \frac{1}{2} h\nu_0 - \frac{h\nu_0 e^4}{2f^2 r^6} + \dots \ . \qquad (2.15)$$

Hence, the pair energy is

$$u(r) = -\frac{h\nu_0 e^4}{2f^2 r^6} + \dots \ , \qquad (2.16)$$

which is attractive.

In three dimensions

$$u(r) = -\frac{3h\nu_0 e^4}{4f^2 r^6} + \dots \ . \qquad (2.17)$$

We can put this in a more convenient form by writing

$$h\nu_u \cong I \ , \tag{2.18}$$

where I is the ionization potential, and

$$\alpha = \frac{e^2}{f} \ , \tag{2.19}$$

where α is the polarizability of the molecule. We can obtain Eq. (2.19) by writing for the instantaneous dipole moment

$$\mu = ex = \alpha E \ , \tag{2.20}$$

where E is the instantaneous electric field producing the displacement x. Equating forces

$$fx = eE \ . \tag{2.21}$$

Equations (2.20) and (2.21) give (2.19). Substitution of (2.18) and (2.19) into (2.17) gives

$$u(r) = -\frac{3I\alpha^2}{4r^6} + \cdots \ . \tag{2.22}$$

If the molecules are of different species

$$u(r) = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\frac{\alpha_1\alpha_2}{r^6} + \cdots \ . \tag{2.23}$$

If more terms in the expansion of the ground state energy are retained

$$u(r) = -\frac{c_6}{r^6} - \frac{c_8}{r^8} - \frac{c_{10}}{r^{10}} + \cdots \ , \tag{2.24}$$

where the coefficients c_6, c_8,$\cdots$ can be calculated form measurable molecular properties by formula analogous to Eq. (2.23).

The repulsive forces at short separation result from Pauli exclusion principle interactions between the overlapping electron clouds. Hartree-Fock calculations indicate that these short range forces are approximately exponential functions of the separation.

Using the fact and Eq. (2.24), Barker(1) has used

$$u(x)/\varepsilon = \left\{ \sum_{i=0}^{5} A\ (x-1)^{i} \right\} \exp\{12.5(1-x)\} - \sum_{j=0}^{2} c_{2j+6}/(0.01 + r^{2j+6}), \tag{2.25}$$

where ε is the depth of the potential at its maximum (where $r = r_m$) and $x = r/r_m$. Barker obtained c_6, c_8, and c_{10} from analogous to Eq. (2.23) and fit the A_i, ε , and r_m a wide range of experimental data. For argon, he obtained $\varepsilon/k = 142.1$K and $r_m = 3.7612$ Å. The value of r for which Barker's argon potential changes sign is $\sigma = 3.3605$ Å. Barker's potential is plotted in Fig. 1. Barker has made similar determinations of the pair interactions of the other inert gas molecules.

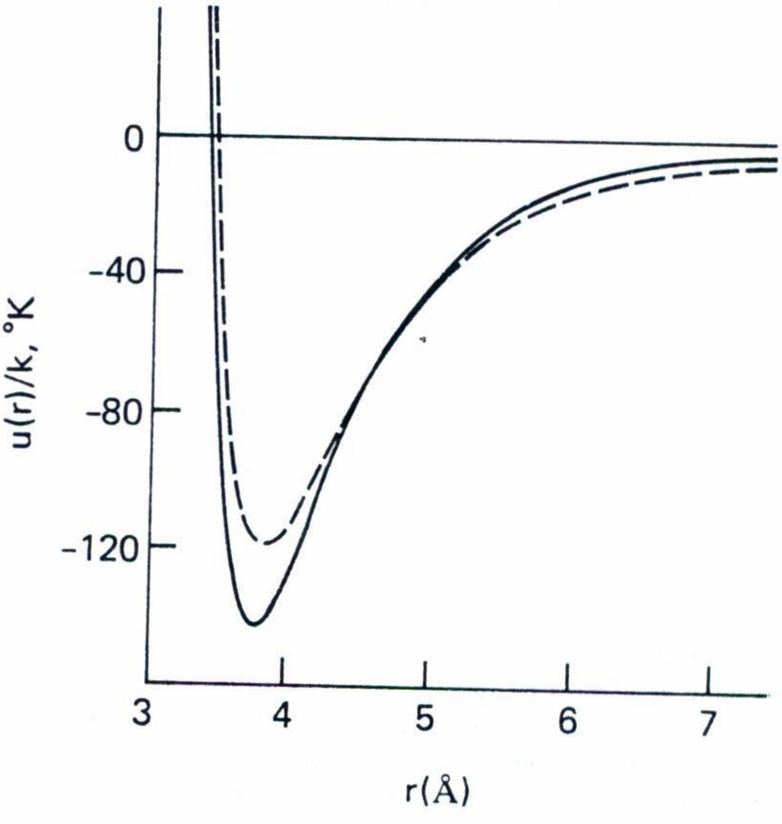

Fig. 1. The argon-argon pair interaction potential. The solid curve is Barker's potential and the broken curve is the 6:12 potential with $\varepsilon/k = 119.8$°K and $\sigma = 3.405$ Å.

An argument similar to that used to obtain Eq. (2.23) shows that for triplet interactions, when all three molecules are far apart,

$$w(r_{12},r_{13},r_{23}) = \nu \frac{1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3}{r_{12}^3 r_{13}^3 r_{23}^3} \quad , \qquad (2.26)$$

where the r_{ij} and θ_i are the three sides and angles of the triangle formed by the three molecules.

Very little is known about the form of $w(r_{12},r_{13},r_{23})$ when one or more of the intermolecular distances is small. However, all available evidence indicates that Eq. (2.26) gives the important contributions to w. Evidently, the repulsive terms in $u(r_{ij})$ prevent the molecules from being in configurations where deficiencies in Eq. (2.26) are observable.

As has been mentioned, u(r) and w(r,s,t) are known only for a few simple molecular pairs and triplets. Fortunately, for most systems, the properties of the system are not sensitive to the details of the potential interactions. Thus, a lot can be learned from model potentials In all of these model systems, triplet interactions are assumed not to exist. Theoretical calculations are usually compared with computer simulations using Monte Carlo or molecular dynamics methods.

A. *Model Potentials*

The simplest model potential is the hard-sphere potential

$$u_{HS}(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma. \end{cases} \qquad (2.27)$$

A somewhat more realistic potential with attraction as well as repulsion is the square-well potential

$$u(r) = \begin{cases} \infty, & 0 < r < \sigma \\ -\varepsilon, & \sigma < r < \lambda\sigma \\ 0, & r > \lambda\sigma \quad . \end{cases} \qquad (2.28)$$

An even more realistic potential has been proposed by Lennard-Jones. He used $-c_6/r^6$ for the attractive term and represented the repulsive energy by an inverse power of r. Before the advent of digital computers it was convenient to take this repulsive index as twice 6.

Thus, we have the 6-12 potential

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] , \tag{2.29}$$

where ε is the depth of the potential at its minimum and the potential changes sign at $r = \sigma$.

Although originally proposed as a potential for real fluids, the 6-12 potential is not satisfactory for this purpose. For example, it is not possible to fit both the value of c_6 and thermodynamic data. However, with $\varepsilon/k = 119.8°K$ and $\sigma = 3.40\ \mathring{A}$, the 6-12 potential gives the qualitatively satisfactory fit of the properties of dense argon. The Barker and Lennard-Jones potentials for argon are compared in Fig. 1.

The polar molecules, a commonly used potential is the dipolar hard-sphere potential

$$u(r_{12},\underset{\sim}{\mu}_1,\underset{\sim}{\mu}_2) = u_{HS}(r) - \frac{\mu^2}{r_{12}^3} D(1,2), \tag{2.30}$$

where $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$ are the dipole moments of molecules 1 and 2, $\mu = |\underset{\sim}{\mu}_i|$, and

$$D(1,2) = 3(\hat{\mu}_1\cdot\hat{r}_{12})(\hat{\mu}_2\cdot\hat{r}_{12}) - (\hat{\mu}_1\cdot\hat{\mu}_2) \quad . \tag{2.31}$$

In Eq. (2.31) the caret indicates that the vectors are unit vectors.

For charged systems, the charged hard-sphere potential is useful

$$u_{ij}(r) = u_{HS}(r) + \frac{z_i z_j e^2}{\varepsilon r} , \tag{2.32}$$

where $z_i e$ is the charge on ion i (e is the electronic charge) and ε is the dielectric constant of the medium.

There are a great many more model potentials which have been proposed but these are the ones that will be considered in these lectures.

Suppose several substances ($\lambda = 1,2,\cdots$) have the potential functions of the same general form,

$$U_N = \varepsilon_\lambda U_N(r/\sigma_\lambda,\alpha_\lambda,\beta_\lambda\cdots) , \tag{2.33}$$

where ε_λ and σ_λ have the dimensions of energy and length, respectively, and $\alpha_\lambda, \beta_\lambda, \cdots$ are dimensionless parameters. An example, might be $\nu^* = \nu/\varepsilon r_m^9$. Then one can show that the thermodynamic functions are universal functions of reduced temperature $T^* = kT/\varepsilon_\lambda$ and density $\rho^* = \rho\sigma_\lambda^3$ and of the dimensionless parameters α_λ, $\beta_\lambda, \cdots$. We can refer to this observation as the law of corresponding states.

3. FORMALISM-INTEGRAL EQUATIONS

We now obtain some integral equations for fluids. Throughout this and the succeeding sections we assume that the molecules have a large enough mass so that quantum effects can be neglected.

The fundamental result in statistical mechanics is that the probability of finding N molecules in a configuration given by $\mathbf{r}_i$, Ω_i is proportional to

$$\exp\{-\beta U_N\} \ , \tag{3.1}$$

where $\beta = 1/kT$. Thus, if we define $g(1,\cdots,h)$ as the probability of finding any h molecules at $\mathbf{r}_1,\cdots,\mathbf{r}_h$ with orientations $\Omega_1,\cdots,\Omega_h$, normalized so that $g(1,\cdots,h) = 1$ when all the molecules are far apart

$$g(1\cdots h) = V^h \frac{\int \exp\{-\beta U_N\} d\mathbf{r}_{h+1}\cdots d\mathbf{r}_N d\Omega_{h+1}\cdots d\Omega_N}{\int \exp\{-\beta U_N\} d\mathbf{r}_1\cdots d\mathbf{r}_N d\Omega_1\cdots d\Omega_N} \ , \tag{3.2}$$

where $d\mathbf{r}_i$ and $d\Omega_i$ are integration elements. For convenience, we assume that $d\Omega_i$ is normalized so that $\int d\Omega_i = 1$. We have been a little careless with terms of order 1/N in our definition of $g(1\cdots h)$. Despite this Eq. (3.2) is satisfactory for our purposes. We can call $g(1\cdots h)$ the h-body distribution function. The pair distribution function is $g(1,2)$ and the radial distribution function is

$$g(r_{12}) = \int g(1,2) d\Omega_1 d\Omega_2 \ . \tag{3.3}$$

The denominator in Eq. (3.2) is the partition function which is related to the free energy by

$$A = -kT \ln\left[\frac{\lambda^{-3N}}{N!}\int \exp\{-\beta U_N\} d\underset{\sim}{r}_1 \cdots d\Omega_N\right] , \tag{3.4}$$

where $\lambda = h/(2\pi mkT)^{\frac{1}{2}}$ and m is the molecular mass.

Other routes to thermodynamics include the energy equation

$$U = \frac{s}{2} NkT + \frac{1}{2} N\rho \int u(1,2)g(1,2)d\underset{\sim}{r}_2 d\Omega_1 d\Omega_2 , \tag{3.5}$$

where s is the number of kinetic degrees of freedom, the pressure equation

$$\frac{p}{\rho kT} = 1 - \frac{1}{6}\rho\beta \int (\underset{\sim}{r}_1-\underset{\sim}{r}_2)\cdot\underset{\sim}{\nabla} u(1,2)g(1,2)d\underset{\sim}{r}_2 d\Omega_1 d\Omega_2 , \tag{3.6}$$

which for spherical potentials simplifies to

$$\frac{p}{\rho kT} = 1 - \frac{1}{6}\rho\beta \int r\,\frac{du(r)}{dr}\, g(r)d\underset{\sim}{r} , \tag{3.7}$$

and for the hard-sphere potential simplifies even further to

$$\frac{p}{\rho kT} = 1 + \frac{2\pi}{3}\rho\sigma^3 y(\sigma), \tag{3.8}$$

where $y(r) = g(r)\exp[\beta u(r)]$. Lastly there is the compressibility equation

$$\begin{aligned} kT\,\frac{\partial\rho}{\partial p} &= 1 + \rho \int h(1,2)d\underset{\sim}{r}_2 d\Omega_1 d\Omega_2 \\ &= 1 + \rho\int h(r)d\underset{\sim}{r} , \end{aligned} \tag{3.9}$$

where

$$h(1,2) = g(1,2) - 1 \tag{3.10}$$

is the total correlation function. In these equations $\rho = N/V$.

Equation (3.5) and (3.6) are valid only for systems with only pair interactions. There is no such restriction on Eq. (3.9).

It is useful to introduce a new function, c(1,2), the direct correlation function which is related to h(1,2) by the Ornstein-Zernike equation

$$h(1,2) = c(1,2) + \rho\int h(1,3)c(2,3)d\underset{\sim}{r}_3 d\Omega_3 \ . \tag{3.11}$$

Averaging Eq. (3.11) gives

$$h(r_{12}) = c(r_{12}) + \rho\int h(r_{13})c(r_{23})d\underset{\sim}{r}_3 \ . \tag{3.12}$$

Introducing the Fourier transform

$$\tilde{h}(k) = \frac{4\pi}{k}\int_0^\infty rh(r) \sin krdr \tag{3.13}$$

(note that k here is not Boltzmann's constant) and using

$$d\underset{\sim}{r}_3 = 2\pi \frac{r_{13}r_{23}}{r_{12}} dr_{13}dr_{23} \quad , \tag{3.14}$$

gives

$$\tilde{h}(k) = \tilde{c}(k) + \rho\tilde{h}(k)\tilde{c}(k) \tag{3.15}$$

or

$$1 + \rho\tilde{h}(k) = [1 - \rho\tilde{c}(k)]^{-1} \tag{3.16}$$

so that

$$\begin{aligned} \beta \frac{\partial p}{\partial \rho} &= [1 + \rho\tilde{h}(0)]^{-1} + 1 - \rho\tilde{c}(0) \\ &= 1 - \rho\int c(r)d\underset{\sim}{r} \\ &= 1 - \rho\int c(1,2)d\underset{\sim}{r}_2 d\Omega_1 d\Omega_2 \ . \end{aligned} \tag{3.17}$$

A. *Born-Green Equation*

Differentiating (3.2) with respect to $\underset{\sim}{r}_1$ for the case $h = 2$ gives

$$-kt\underset{\sim}{\nabla}_1 g(12) = g(12)\nabla_1 u(12) + \rho\int g(123)\underset{\sim}{\nabla}_1 u(13)d\underset{\sim}{r}_3 . \tag{3.18}$$

Equation (3.18) cannot be solved unless g(123) is approximated. The most common approximation is the superposition approximation of Kirkwood

$$g(123) = g(12)g(13)g(23). \tag{3.19}$$

Substitution of (3.19) into (3.18) gives the Born-Green equation

$$-kT\underset{\sim}{\nabla}_1 \ln g(12) = \underset{\sim}{\nabla}_1 u(12) + \rho\int g(13)g(23)\underset{\sim}{\nabla}_1 u(13)d\underset{\sim}{r}_3 . \tag{3.20}$$

Equation (3.20) has not been too successful in the description of bulk fluids. However, it does have promise in interfacial problems where it satisfies certain exact theorems which we will mention later.

B. *Hypernetted Chain Approximation*

If some approximate relation between h(12) and c(12) were coupled with the Ornstein-Zernike equation, Eq. (3.11), an approximate integral equation would be obtained.

Two such integral equations can be obtained by considering the expansion of g(r) in powers of ρ:

$$e^{\beta u_{12}} g_{12} = 1 + \rho\int f_{13}f_{23}d\underset{\sim}{r}_3 + \cdots \tag{3.21}$$

or equivalently

$$\ln g_{12} + \beta u_{12} = \rho\int f_{13}f_{23}d\underset{\sim}{r}_3 + \cdots, \tag{3.22}$$

where $f_{ij} = e^{-\beta u_{ij}} - 1$. The integral in (3.21) and (3.22) looks very much like the integral in the Ornstein-Zernike equation (since the leading term in the expansion of both h_{ij} and c_{ij} is f_{ij}). In fact equating the integral in (3.21) to that in the Ornstein-Zernike equation gives the Percus-Yevick approximation

$$g(r)e^{\beta u(r)} = 1 + h(r) - c(r) \quad , \tag{3.23}$$

and equating the integral in (3.22) to that in the Ornstein-Zernike equation gives the hypernetted chain approximation

$$\ln g(r) + \beta u(r) = h(r) - c(r). \tag{3.24}$$

The Percus-Yevick equation gives good results for hard spheres. We will summarize these results in the next section. Unfortunately, the Percus-Yevick equation is much less successful for longer-ranged potentials. The hypernetted chain approximation although less successful for hard-spheres, is very successful for other potentials, in particular for the Coulomb potential.

C. *Mean Spherical Approximation*

The mean spherical approximation is a linearizad version of the hypernetted chain approximation for potentials with a hard core. We can derive this approximation by assuming that ouside the hard core $(r > \sigma) h = g - 1$ is small compared to unity and expanding In g in Eq. (3.24) Thus

$$c(r) = -\beta u(r) \qquad (r > \sigma) \quad , \tag{3.25}$$

which when coupled with the exact condition

$$g(r) = 0 \qquad (r < \sigma) \quad , \tag{3.26}$$

and the Ornstein-Zernike equation gives an integral equation which is remarkably useful.

For the hard-sphere potential, Eq. (3.25) becomes

$$c(r) = 0 \qquad (r > \sigma) \quad . \tag{3.27}$$

For hard-spheres, the mean spherical and Percus - Yevick approximations are equivalent. Interesting the solution of these approximations for hard spheres is accurate and analytic. A fairly simple outline of the solution of the Percus-Yevick/mean spherical approximation for hard spheres can be found in Chapter 12 of Statistical Mechanics and Dynamics(2).

The Laplace transform of the radial distribution function, which can be inverted analytically, is

$$\begin{aligned} G(s) &= \int_\sigma^\infty r g(r) e^{-sr} dr \\ &= \frac{sL(s)}{12\eta[L(s) + e^{s}S(s)]} \quad , \end{aligned} \tag{3.28}$$

where

$$L(s) = 12\eta[1 + 2\eta + (1 + \eta/2)s] \tag{3.29}$$

and

$$S(s) = -12\eta(1 + 2\eta) + 18\eta^2 s + 6\eta(1-\eta)s^2 + (1-\eta)^2 s^3 \ , \tag{3.30}$$

where $\eta = \pi\rho\sigma^3/6$. The pressure and compressibility equations isotherms are

$$\frac{p}{\rho kT} = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2} \tag{3.31}$$

and

$$\frac{p}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \ . \tag{3.32}$$

These isotherms are compared with computer simulation results in Fig. 2. The two isotherms lie on either side of the simulation results. Interestingly a linear combination

$$\frac{p}{\rho kT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \ , \tag{3.33}$$

due to Carnahan and Starling, agrees well with the simulation results.

The Percus-Yevick/mean spherical approximation $g(r)$ is compared with simulation results in Fig. 3. The agreement is good.

For other systems, the mean spherical approximation is no longer equivalent to the Percus-Yevick approximation. Except at low densities, the mean spherical approximation generally seems more reliable than the Percus-Yevick approximation. The mean spherical approximation often yields analytic results.

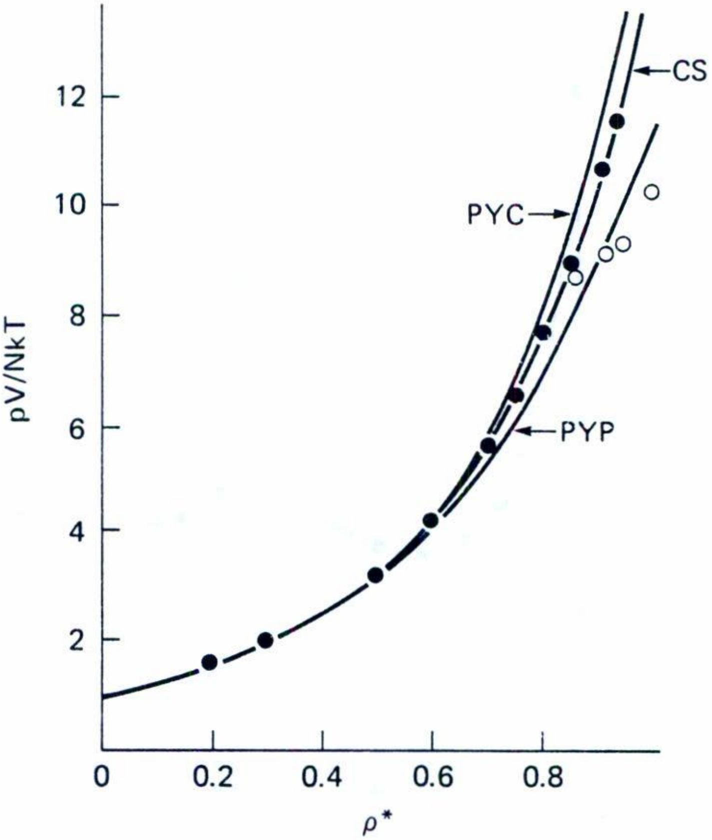

Fig.2. Equation of state of the hard-sphere fluid. The solid and open circles give the machine simulation values for fluid and solid hard-spheres, respectively. The curves marked PYP, PYC, and CS give the results of Eqs.(3.31), (3.32), and (3.33), respectively. The reduced density $\rho^* = \rho\sigma^3$.

Further results and references can be found in the review of Barker and Henderson(3).

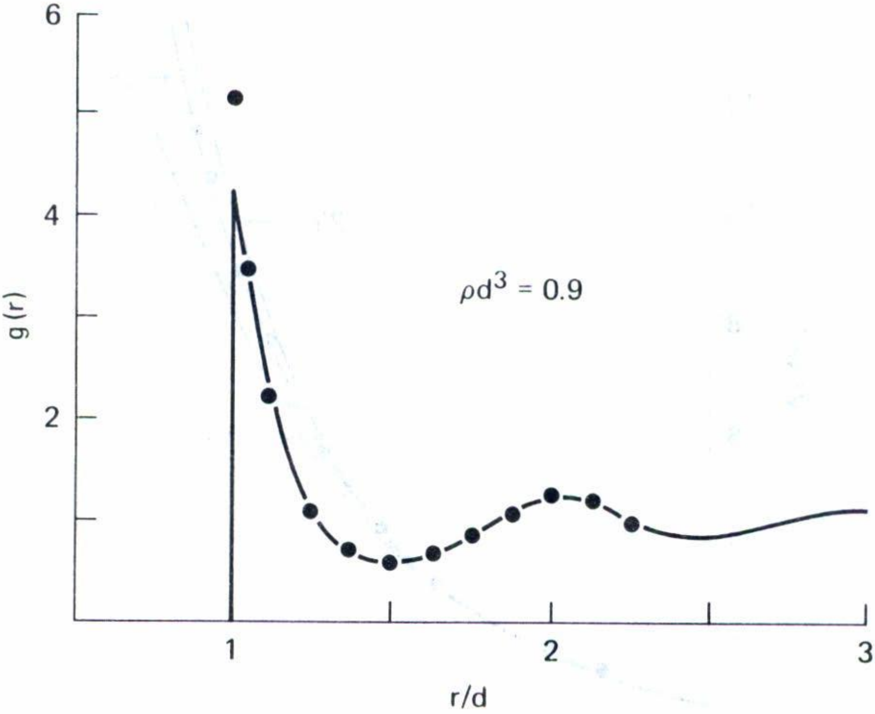

Fig. 3. Radial distribution function for the hard-sphere fluid. The points give the machine simulation values, the curves give the results obtained by inverting Eq. (3.28). The parameter d is the hard-sphere diameter.

4. FORMALISM-PERTURBATION THEORY

Our starting point is the free energy. For a potential which does not depend on orientations, the free energy is

$$A = -kT \int \prod_{i<j} e_{ij} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N \quad + \text{ terms independent of density,} \quad (4.1)$$

where we have assumed that the potential is additive and $e_{ij} = \exp[-\beta u_{ij}]$. Further, assume that e_{ij} depends upon a parameter γ, i.e.,

$$e(r) = e(\gamma;r) \quad , \tag{4.2}$$

which is small enough so that the free energy can be expandend in a series in γ:

$$A = A_0 + \gamma \left.\frac{\partial A}{\partial\gamma}\right|_{\gamma=0} + \frac{1}{2}\gamma^2 \left.\frac{\partial^2 A}{\partial\gamma^2}\right|_{\gamma=0} + \cdots , \tag{4.3}$$

where A_0 is the free energy of the reference or unperturbed system, for which $\gamma = 0$.

Thus,

$$\beta \frac{\partial A}{\partial\gamma} = -\frac{1}{2}\rho^2 \int g(12)e_\gamma(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \tag{4.4}$$

and

$$\begin{aligned}\beta \frac{\partial^2 A}{\partial\gamma^2} = & -\frac{1}{2}\rho^2 \int g(12)e_{\gamma\gamma}(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \\ & - \rho^3 \int g(123)e_\gamma(12)e_\gamma(23)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 \\ & - \frac{1}{4}\rho^2 \int [g(1234) - g(12)g(34)]e_\gamma(12)e_\gamma(34)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 d\underset{\sim}{r}_4 ,\end{aligned} \tag{4.5}$$

where

$$e_\gamma = e^{-1}\frac{\partial e}{\partial\gamma} \quad , \tag{4.6}$$

$$e_{\gamma\gamma} = e^{-1}\frac{\partial^2 e}{\partial\gamma^2} \quad . \tag{4.7}$$

In the limit $\gamma = 0$ the functions $g(1\cdots h)$ are the reference fluid distribution functions.

Equations (4.5) is valid only in the canonical ensemble. An extra term must be added to obtain results wich are valid in the thermodynamic limit ($N\to\infty$, $V\to\infty$, ρ fixed). However, this correction term is not relevant for our present discussion. Details can be found in Barker and Henderson(3).

The corresponding results for the radial distribution function are

$$g(r) = g_0(r) + \gamma \left.\frac{\partial g(r)}{\partial\gamma}\right|_{\gamma=0} + \cdots , \tag{4.8}$$

where

$$\frac{\partial g(12)}{\partial\gamma} = g(12)e_{\gamma}(12) + 2\rho\int g(123)e_{\gamma}(23)d\underset{\sim}{r}_3$$
$$+ \frac{1}{2}\rho^2\int[g(1234) - g(12)g(34)]e_{\gamma}(34)d\underset{\sim}{r}_3 d\underset{\sim}{r}_4 \ . \tag{4.9}$$

Similary there is a correction term for the thermodynamic limit. For details see Barker and Henderson(3).

Equation (4.5) is often difficult to use. A similar approximation,based on the superposition approximation, is

$$\beta\frac{\partial^2 A}{\partial\gamma^2} = -\frac{1}{2}\rho^2\int g(12)e_{\gamma\gamma}(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2$$
$$- \rho^3\int g(12)g(23)e_{\gamma}(12)e_{\gamma}(23)h(13)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 d\underset{\sim}{r}_3$$
$$- \frac{1}{4}\rho^4\int g(12)g(34)e_{\gamma}(12)e_{\gamma}(34)$$
$$\times\ [2h(13)h(24) + 4h(13)h(14)h(24) + h(13)h(14)h(23)h(24)\ ]d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 d\underset{\sim}{r}_4 \tag{4.10}$$

Although approximate, Eq. (4.10) is applicable to an infinite system.

The higher-order terms involve many integrals. At least for our discussion, the important terms in third and fourth-order are

$$\beta\frac{\partial^3 A}{\partial\gamma^3} = -\frac{1}{2}\rho^2\int g(12)e_{\gamma\gamma\gamma}(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2$$
$$-\rho^3\int g(123)e_{\gamma}(12)e_{\gamma}(13)e_{\gamma}(23)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots, \tag{4.11}$$

$$\beta\frac{\partial^4 A}{\partial\gamma^4} = -\frac{1}{2}\rho^2\int g(12)e_{\gamma\gamma\gamma\gamma}(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2$$
$$- 3\rho^4\int g(1234)e_{\gamma}(12)e_{\gamma}(13)e_{\gamma}(24)e_{\gamma}(34)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 d\underset{\sim}{r}_4 + \cdots, \tag{4.12}$$

where

$$e_{\gamma\gamma\gamma} = e^{-1}\frac{\partial^3 e}{\partial\gamma^3} \quad , \tag{4.13}$$

etc. The first terms in Eqs. (4.11) and (4.12) are necessary for the correct limiting behavior at low densities. The second terms in Eqs. (4.11) and (4.12) are called ring or chain diagrams because, if the f functions are regarded as links in a diagram, the sequence of f's forms a simple closed chain.

In general, there are three functional dependencies of $e(\gamma;r)$ on γ which have been considered. The first it

$$e(\gamma;r) = \exp[-\beta\{u_0(r) + \gamma u_1(r)\}] \quad , \tag{4.14}$$

where u_0 is the pair-potential of the reference system. Hence

$$e_{\gamma}(r) = -\beta u_1(r) \tag{4.15}$$

and

$$e_{\gamma\gamma}(r) = \{\beta u_1(r)\}^2 \quad , \tag{4.16}$$

$$e_{\gamma\gamma\gamma}(r) = -\{\beta\, u_1(r)\}^3 \quad , \tag{4.17}$$

etc. This case is useful when the perturbation energy $u_1(r) = u(r) - u_0(r)$ is small.

We shall see that this form of the perturbation expansion is useful for simple fluids. For such applications the firs-order term is dominant and gives the average contribution of the perturbation energy $u_1(r)$. The higher-order terms are small and are fluctuation terms which are small if the reference fluid resists changes in structure. Since macroscopic fluctuations are proportional to the compressibility, Barker and Henderson have suggested that a useful approximation might be

$$\frac{\partial^2 A}{\partial\gamma^2} = -\frac{1}{2}\beta\rho^2\left(\frac{\partial\rho}{\partial p}\right)_T \int g(12)u_1^2(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \ . \tag{4.18}$$

At low densities $\partial\rho/\partial p = \beta$. Thus, Eq. (4.18) gives the correct low density behavior. For reference fluids with a steep repulsion, $\partial\rho/\partial p \to 0$ at high densities and the fluctuation correction is small, as required.

Shortly we will see that for the lattice gas,

$$\frac{\partial^2 A}{\partial\gamma^2} = -\frac{1}{2}\rho^2\left(\frac{\partial\rho}{\partial p}\right)_T^2\int g(12)u_1^2(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \tag{4.19}$$

is exact. This suggests that another approximation which may have some advantages over the original Barker-Henderson compressibility approximation would be obtained replacing $u_1(r)$ by $kT(\partial\rho/\partial p)u_1(r)$ in the low density and other important terms. Thus,

$$\frac{\partial^3 A}{\partial\gamma^3} = \frac{1}{2}\rho^2\left(\frac{\partial\rho}{\partial p}\right)^3\int g(12)u_1^3(12)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2$$

$$+\rho^3\left(\frac{\partial\rho}{p}\right)^3\int g(123)u_1(12)u_1(13)u_1(23)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 d\underset{\sim}{r}_3, \tag{4.20}$$

etc.

In some applications $u_1(r)$ is large and positive. For such applications $e_\gamma(r)$, given by Eq. (4.15), is not small. Then it may be more appropriate to sue

$$e(\gamma;r) = e_0(r) + \gamma e_0(r)f_1(r) , \tag{4.21}$$

where

$$e_0(r) = \exp\{-\beta u_0(r)\} , \tag{4.22}$$

$$f_1(r) = \exp\{-\beta u_1(r)\} - 1 . \tag{4.23}$$

In the above equations, $u_0(r)$ is the reference pair-potential and $u_1(r) = u(r) - u_0(r)$. For this case

$$e_\gamma(r) = e^{-1}e_0 f_1(r) , \tag{4.24}$$

so that

$$e_\gamma(r)\Big|_{\gamma=0} = f_1(r) , \tag{4.25}$$

and

$$e_{\gamma\gamma}(r) = 0 , \tag{4.26}$$

$$e_{\gamma\gamma\gamma}(r) = 0 \quad , \tag{4.27}$$

etc. If $u_1(r)$ is large and positive, $e_\gamma(r)$ is boundend. In principle, this approach could be used with large and negative perturbations. However, for this situation, $e_\gamma(r)$ would then be very large and this approach would be of limited value.

A third procedure, also applicable to potentials which are large and positive, is based upon

$$e(\gamma;r) = \exp\left\{ -\beta u \left(d + \frac{r-d}{\gamma}\right)\right\} \quad . \tag{4.28}$$

This gives an expansion in a inverse steepness parameter, using a hard-sphere reference fluid, where d is the hard-sphere diameter. Expansions based upon Eq. (4.28) are useful when u(r) is large, positive, and steep. Thus

$$e_\gamma(r) = \beta u' \left(d + \frac{r-d}{\gamma}\right) \frac{r-d}{\gamma^2} \quad . \tag{4.29}$$

A perturbation theory for a given system is developed by making a choice as to what is an appropriate reference fluid and which of the three procedures is to be used. Other choices besides the above three are possible. The above are just those which are commonly used. Generally, a hard-sphere fluid is used as the reference system.

A. *Virial Expansion*

The simplest reference fluid is the perfect gas, where $g(1\cdots h)=1$. If we used the perfect gas as a reference fluid then the perturbation is the entire potential. Obviously, the u-expansion of Eqs. (4.25) to (4.17) is inappropriate. It is better to use the f-expansion of Eqs. (4.21) to (4.27). Because the $g(1\cdots h)$ all equal unity, the superposition approximation is valid and Eq. (4.10) is free of approximation. Hence, since $e_{\gamma\gamma} = 0$, etc., and $h_0(r) = 0$, we have, using Eq. (4.10) but uncluding the fifth-order term

$$\frac{A-A_0}{nKt} = -\frac{1}{2}\rho\int f_{12}d\underset{\sim}{r}_2 - \frac{1}{6}\rho^2\int f_{12}f_{13}f_{23}d\underset{\sim}{r}_2 d\underset{\sim}{r}_3$$

$$- \frac{1}{8}\, \rho^3 \int f_{12} f_{13} f_{24} f_{34}\, d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \;-\; \frac{1}{4}\, \rho^3 \int f_{12} f_{13} f_{14} f_{24} f_{34}\, d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$- \frac{1}{10}\, \rho^4 \int f_{12} f_{15} f_{23} f_{34} f_{45}\, d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + \cdots , \tag{4.30}$$

where $f_{12} = f(r_{12}) = \exp\{-\beta u(r_{12})\} - 1$. The last two terms are the fourth order term.

If the terms in Eq. (4.30) are grouped in powers of ρ rather than by the number of f-functions, Eq. (4.30) is the virial expansion of A. The virial expansion is the simplest form of a perturbation theory.

B. *Lattice Gas*

Another simple application of perturbation theory is obtained by considering the lattice gas in which the N molecules are restricted to L lattice sites.

For this system

$$u(r) = \begin{cases} \infty , & r = 0 \\ -\varepsilon , & r = \text{nnd} \\ 0 , & \text{otherwise,} \end{cases} \tag{4.31}$$

where nnd means the nearest neighbor distance.

The unperturbed system is a lattice gas of noninteracting molecules, subject only to the restriction that only one molecule can occupy a lattice site. Thus,

$$\frac{A_0}{NkT} = \ln x + \frac{1-x}{x} \ln (1-x), \tag{4.32}$$

where $x = N/L$ plays the role of the density. Differentiating,

$$\beta p_0 = - \ln(1-x) , \tag{4.33}$$

$$\beta \frac{\partial p_0}{\partial x} = \frac{1}{1-x} . \tag{4.34}$$

Since the perturbation potential is small and negative, the u-expansion can be used. The $g(1 \cdots h)$ of the reference fluid are equal to unity when all the molecules occupy different sites and are zero otherwise. As a result, the reference $g(1\cdots h)$ satisfy the superposition approximation and Eq. (4.10) can be used without approximation.

To evaluate the terms in the expansion we note that, in the limit $\gamma = \beta\varepsilon = 0$, $h(12) = 0$ unless molecules 1 and 2 are on the same site and $u_1(12)g(12)$ is zero unless molecules 1 and 2 are nearest neighbors. If z is the number of nearest neighbors of the lattice

$$\left.\frac{\partial(A/NkT)}{\partial(\beta\varepsilon)}\right|_{\beta\varepsilon=0} = -\frac{1}{2}\,xz \tag{4.35}$$

and

$$\left.\frac{\partial^2(A/NkT)}{\partial(\beta\varepsilon)^2}\right|_{\beta\varepsilon=0} = -\frac{1}{2}\,x(1-x)^2 z\ . \tag{4.36}$$

We note by comparing Eqs. (4.34) and (4.36) that Eq. (4.36) could be obtained from Eq. (4.19).

In third order

$$\left.\frac{\partial^3(A/NkT)}{\partial(\beta\varepsilon)^3}\right|_{\beta\varepsilon=0} = -\frac{1}{2}\,x(1-x)^2(1-2x)^2\, z - x^2(1-x)^3\xi, \tag{4.37}$$

where ξ is the number of triangles of nearest neighbors that can be formed on the lattice divided by N. Equation (4.20) does not give Eq. (4.37) exactly but it does give the larger ring diagram correctly and is correct in the limit of low density.

The first-order term is the van der Waals theory result. To this order the perturbation contribution changes the energy of the lattice gas without changes in entropy or structure. The higher-order terms give the effects on the free energy of changes in structure resulting from the perturbation.

The higher-order terms become small at high densities where $L \sim N$. This is because the lattice is nearly fully occupied and rearrangements in structure are difficult since only one molecule can occupy a lattice site. This means that at high densities the perturbation expansion will converge rapidly even if $\beta\varepsilon$ is not small. This is a very important observation. It is not true for many other systems and is one of the main reason why perturbation theory is so useful.

At lower densities, the perturbation expansion converges slowly. Thus, if the expansion is to be used in the neighborhood of the critical point, many terms are needed. For the lattice gas these terms can be obtained fairly easily. For other systems this is not true and so it is only for the lattice gas that critical point properties can be examined. This is one reason why the lattice gas is of such great interest.

5. APPLICATION TO SIMPLE FLUIDS

For a simple liquid consisting of spherical molecules with a steep repulsion, an appropriate reference potential is the positive part of the potential. Thus, using the u-expansion

$$\frac{A-A_0}{NkT} = 2\pi\beta\rho\int_\sigma^\infty u(r)g_0(r)r^2dr + \cdots , \tag{5.1}$$

where A_0 and $g_0(r)$ are the free energy and radial distribution function of the reference fluid and σ is the value of r for which $u(r) = 0$.

The integral in Eq. (5.1) is very nearly independent of density and temperature. Thus, the first-order term has, to a good approximation, the lattice gas form given in Eq. (4.35). The second-order term is also similar to the lattice gas result, Eq. (4.36). In particular, it is small at high densities.

Because, the reference potential is steep, the higher-order terms will be small at high densities, just as was the case for the lattice gas. Even with just the first-order term, the perturbation series gives good results at high densities. With two terms excellent results are obtained at high densities. Even at lower densities the results are quite good.

Despite these results, the perturbation theory outlined above is not very practical since because, in the above form, A_0, $g_0(r)$, and the higher-order distribution functions must be determined by computer simulations for every state which is considered. One might as well perform the computer simulations for the actual system.

The step which actually makes perturbation theory practical for simple liquids is the replacement of A_0 and $g_0(r)$ by the hard-sphere A_{HS}

and $g_{HS}(r)$. Using Eq. (4.29) for $0 \leqq r \leqq \sigma$, Barker and Henderson have shown that

$$A_0 \cong A_{HS} \tag{5.2}$$

and

$$g_0(r) \cong g_{HS}(r) \tag{5.3}$$

if the hard-sphere diameter is chosen by

$$d = \int_0^\infty [1-\exp\{-\beta u_0(z)\}]dz \ . \tag{5.4}$$

Since the thermodynamic properties and distribution functions of hard-spheres are well-known, perturbation theory (with a hard-sphere reference fluid) becomes a simple and accurate theory of liquids. We can obtain A_0 and $g_0(r)$ either form the Percus-Yevick/mean spherical approximation or from computer simulations.

If the integral in Eq. (5.1) is assumed to be independent of the density and temperature and if higher-order terms are neglected, we obtain

$$\frac{A - A_0}{NkT} = - \beta\rho a \tag{5.5}$$

or

$$\frac{p}{\rho kT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \beta\rho a \ . \tag{5.6}$$

This is the van der Waals' equation of state.

Perturbation theory leads to a simple picture of a liquid. At high densities, where the molecules are packed close together, the liquid molecules behave as gas molecules at the same density. The main contribution of the perturbation is to provide the potential well in which the molecules move.

Results for the equation of state of the 6:12 fluid are given in Fig. 4. The agreement of perturbation theory with computer simulation results is excellent. The perturbation theory results shown in Fig. 4 are based on first and second-order terms which are calculated from computer simulations using exact formulae. Very similar results would be obtained if Eqs. (4.18) or (4.19) were used for the second-order terms. Presumably, even better results could be obtained at low densities if formulae like Eq. (4.20) were used for the higher-order terms.

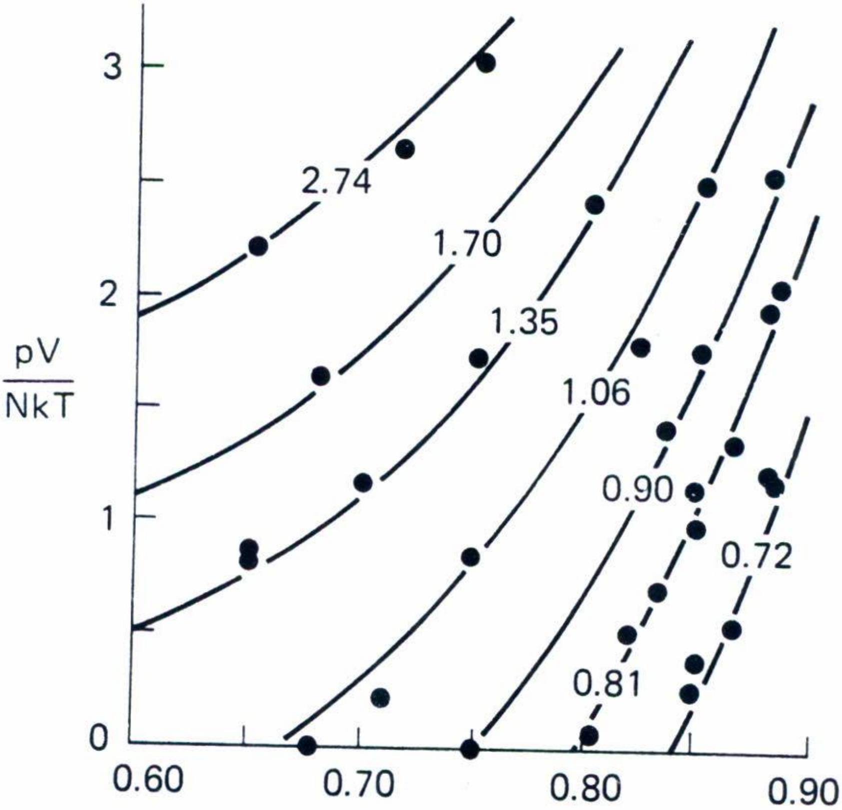

Fig. 4. Equation of state of the 6:12 fluid. The points and curves give the computer simulation and second-order perturbation theory results for seven isotherms that are labelled with the appropriate values of kT/ε.

6. APPLICATION TO ELECTROLYTES

A system of charged hard-spheres, where

$$u_{ij}(r) = u_{HS}(r) + \frac{z_i z_j e^2}{\varepsilon r} \quad , \tag{6.1}$$

is a useful model ionic fluid. In Eq. (6.1), $z_i e$ is the charge of an ion of species i, ε is the dielectric constant of the solvent which is taken to be a dielectric continuum, and σ is the diameter of the hard-spheres. A slightly more general model could be obtained by allowing different ions to have different diameters. In order to keep the discussion as simple as possible, we will not do that here.

Because of charge neutrality

$$\sum_i z_i \rho_i = 0 \ . \tag{6.2}$$

In Eq. (6.2) $\rho_i = N_i/V$ is the density of ions of species i.

The model can be made considerably more general by using a molecular model for the solvent. We defer a discussion of such a model until molecular liquids are considered in the next section.

Waisman and Lebowitz$^{(4)}$ and Blum$^{(5)}$ have applied the mean spherical approximation to the charged hard-sphere system. They find that

$$g_{ij}(r) = g_0(r) - \frac{\beta z_i z_j e^2}{\varepsilon(1 + \Gamma\sigma)^2} \frac{f(r - \sigma)}{r} \qquad (r \geq \sigma) \ , \tag{6.3}$$

where $g_0(r)$ is the hard-sphere radial distribution function, given by Eq. (3.28), Γ is defined by the relation

$$\kappa = 2\Gamma(1 + \Gamma\sigma) \quad , \tag{6.4}$$

where κ is the Debye parameter, defined by

$$\kappa^2 = \frac{4\pi\beta e^2}{\varepsilon} \sum_i z_i^2 \rho_i, \tag{6.5}$$

and the Laplace transform of f(x) is

$$F(s) = \int_0^\infty e^{-sx} f(x) dx$$

$$= \frac{s}{s^2 + 2(\Gamma\sigma)s + 2(\Gamma\sigma)^2(1 - e^{-s})} \quad . \tag{6.6}$$

Equation (6.6) can be inverted analytically(6).

At low concentrations, $\kappa\sigma$ and $\Gamma\sigma$ are small. Equivalently, we can set $\sigma = 0$. Thus, $\Gamma = \kappa/2$ and

$$F(s) = \frac{1}{s + \kappa} \quad , \tag{6.7}$$

so that

$$g_{ij}(r) = 1 - \frac{\beta z_i z_j e^2}{\varepsilon r} e^{-\kappa I} \, , \tag{6.8}$$

where $r \geqq 0$. Equation (6.8) was first obtained by Debye and Hückel. The mean spherical approximation is an extension of the Debye-Hückel theory to higher concentrations (or nonzero σ). The parameter κ is an inverse screening parameter. That is κ^{-1} is a measure of the distance over which the ionic potential is nonzero before the screening of neighboring clouds of ions of opposite sign screen the interaction.

Both Eqs. (6.3) and (6.8) share the difficulty that $g_{ij}(r)$ can become negative for the like pairs. This is a result of the linearization inherent in both the Debye-Hückel and mean spherical approximations and can be overcome by using a nonlinear approximation such as the hypernetted chain approximation.

The mean spherical approximation $g_{ij}(r)$ are compared with the hypernetted chain(7) and computer simulation(8,9) $g(r)$ for a low and a high concentration in Figs. 5 and 6. The mean spherical approximation $g(r)$ is considerably better at high concentrations. Even though the low concentration $g_{ij}(r)$ are unsatisfactory, the difference is given with fair accuracy. Since the thermodynamics depends on this difference rather than upon the absolute values of the $g_{ij}(r)$, the mean spherical approximation thermodynamic function are fairly good even at low concentrations.

The energy in the mean spherical approximation can be calculated from Eq. (3.5). The result is

$$\frac{E_i}{NkT} = - \frac{(2\Gamma)^3(1 + \Gamma\sigma)}{8\pi\rho} \quad , \tag{6.9}$$

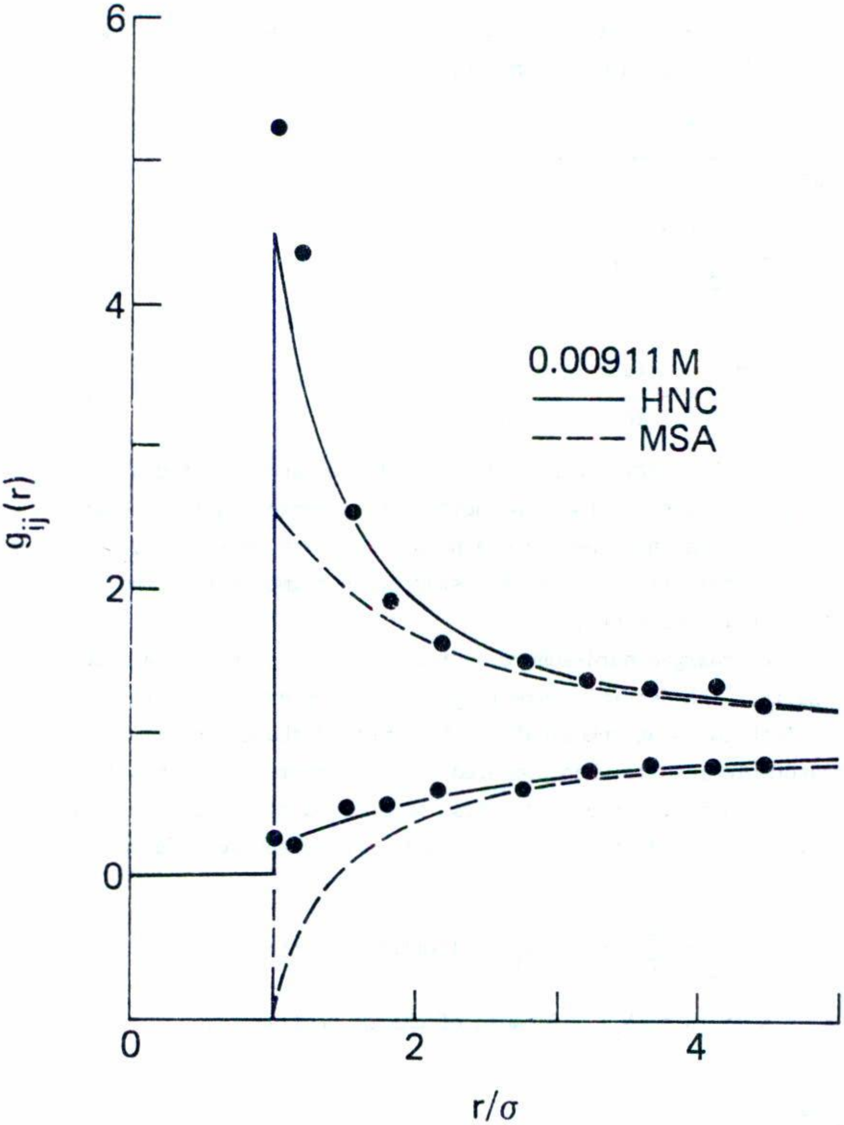

Fig. 5. Radial distribution functions for the charged hard-sphere/continuum dielectric model of a 1:1 electrolyte at 298°K, $\sigma = 4.25\text{Å}$, and $\varepsilon = 78.5$. The points give the computer simulation results.

where $\rho = N/V$ ($N = \sum_i N_i$) is the density of all the hard-spheres and $E_i = E - 3NkT/2$ is the internal energy. From Eq. (6.9)

$$\frac{A - A_0}{NkT} = -\frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} \quad , \tag{6.10}$$

$$\frac{p - p_0}{\rho kT} = -\frac{(2\Gamma)^3}{24\pi\rho} \quad , \tag{6.11}$$

and

$$\beta\,\frac{\partial(p - p_0)}{\partial\rho} = -\frac{(2\Gamma)^3}{16\pi\rho}\,\frac{1 + \Gamma\sigma}{1 + 2\Gamma\sigma} \quad . \tag{6.12}$$

The MSA internal energy and pressure are plotted and compared with computer simulations and the hypernetted chain approximation results in Figs. 7 and 8. The hypernetted chain approximation works well. The mean spherical approximation is less satisfactory but improves as the concentration is increased.

The charged hard-sphere system can also be used as a model for molten salts. The densities are large and the interactions are very strong. Both the mean spherical and hypernetted chain approximations give reasonable results when compared with computer simulations(10).

Perturbation theory can also be applied to the charged hard sphere system. Using the u-expansion with a hard-sphere reference system,

$$\frac{A - A_0}{NkT} = -\frac{1}{2}\beta\rho\sum_{ij} x_i x_j \int u_{ij}(12)g_0(12)d\mathbf{r}_2 + \cdots \quad , \tag{6.13}$$

where $x_i = N_i/N$ ($N = \sum_i N_i$). Because of charge neutrality,

$$\sum z_i x_i = 0 \quad , \tag{6.2}$$

the first-order term in Eq. (6.13) vanishes.

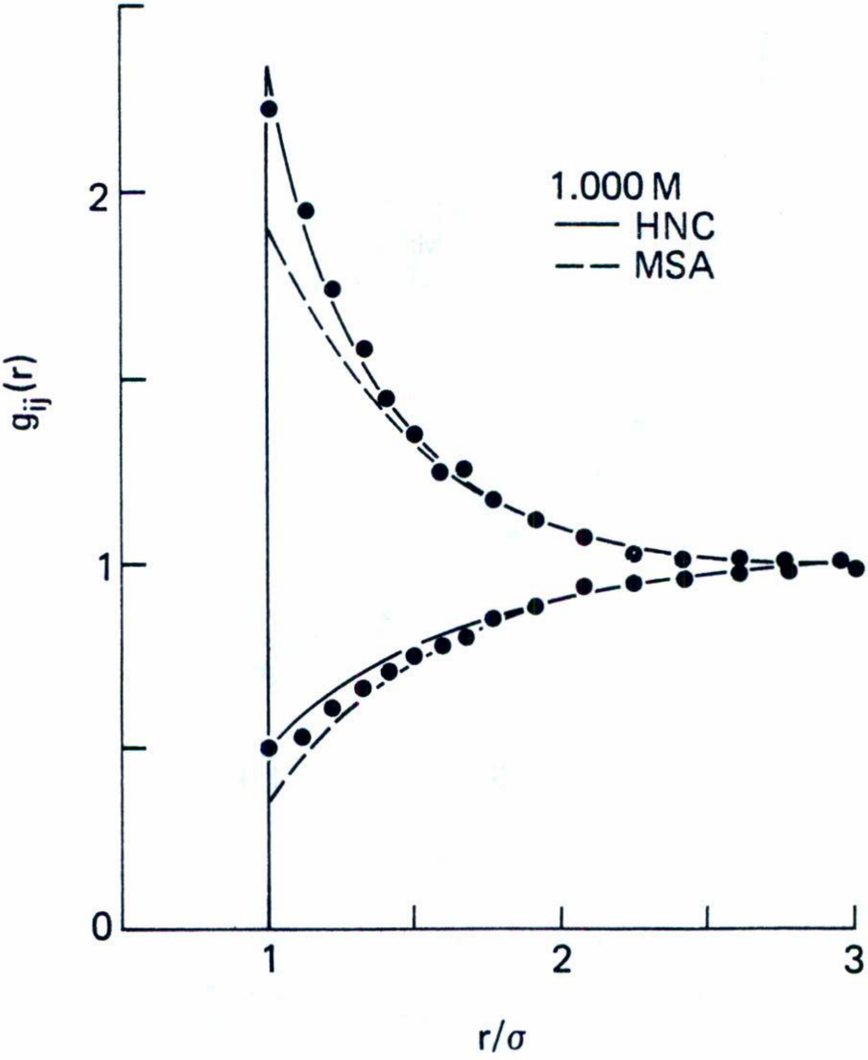

Fig. 6. As in Fig. 5 but with conc = 1.000 M.

In second-order, only the first term in Eq. (4.5) contributes. The other terms vanish because of charge neutrality. Likewise in third-order only the ring diagram is nonzero. Thus,

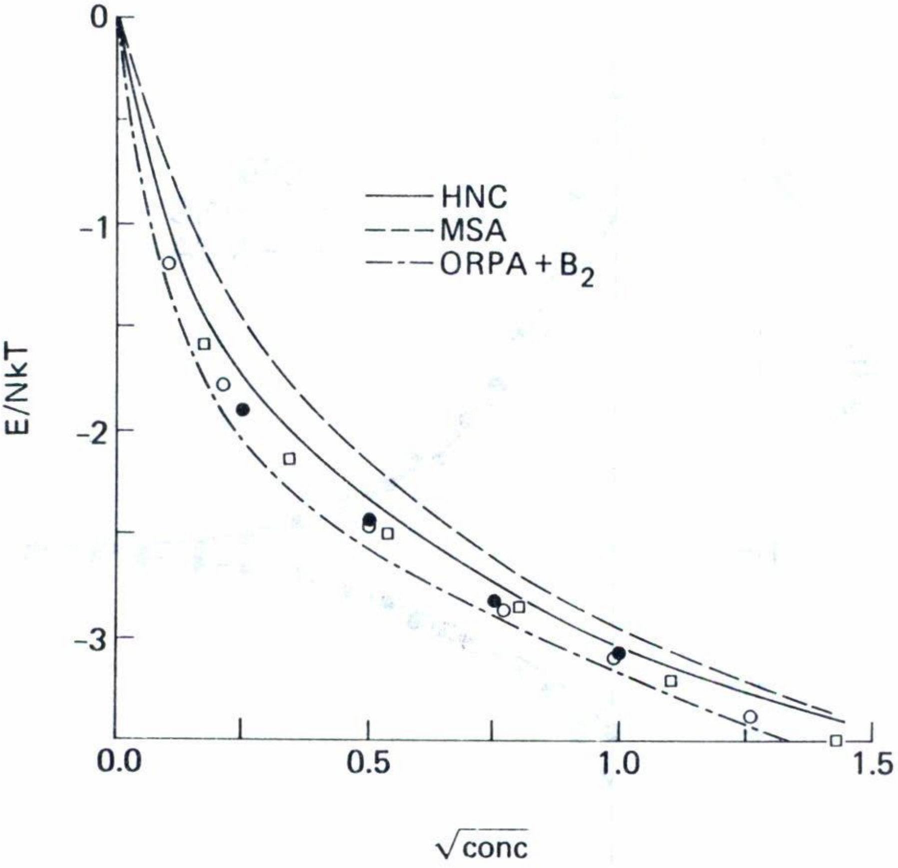

Fig.7. Values of the internal energy for the charged hard-sphere/continuum dielectric model of a 2:2 electrolyte at 298°K, $\sigma = 4.25$ Å, and $\varepsilon = 78.5$. The points marked, ○, ●, and □ give simulation results of Valleau and Cohen, Valleau and Card, and van Megen and Snook, respectively.

$$\frac{A - A_0}{NkT} = -\frac{1}{4}\beta^2\rho\sum_{ij}x_ix_j\int u_{ij}^2(12)g_0(12)d\underset{\sim}{r}_2 + \frac{1}{6}\beta^3\rho^2\sum_{ijk}x_ix_jx_k\int u_{ij}(12)u_{ik}(13)u_{jk}(23)g_0(123)d\underset{\sim}{r}_2d\underset{\sim}{r}_3 + \cdots . \tag{6.14}$$

We see that the cancellation among integrals which leads to small values of the high-order perturbation terms at high densities in the application of perturbation theory to the lattice gas and to simple fluids is not present in this system. Thus, approximations such as Eqs. (4.18) to (4.20) would not be useful for this system. The perturbation series will converge more slowly. None-the-less, we can make progress.

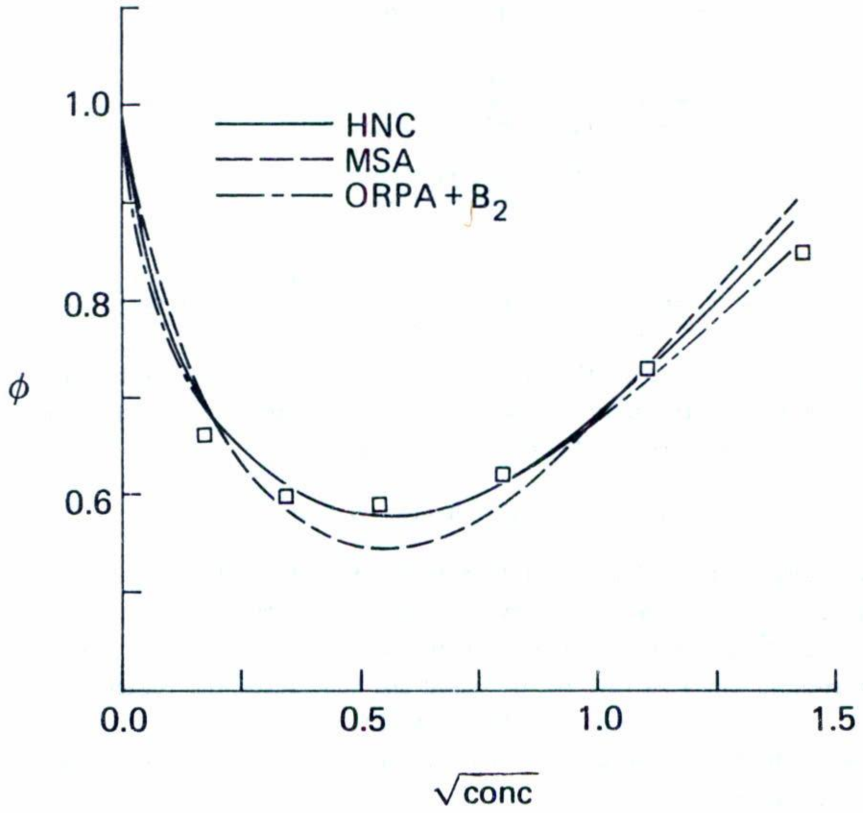

Fig. 8. Values of the osmotic coefficient $\phi = p/\rho kT$ for the charged hard-sphere/continuum dielectric model of a 2:2 electrolyte. The parameters and points are as in Fig. 7.

If we restrict our attention to the symmetric two-component system where $z = |z_1| = |z_2|$, Eq. (6.14) becomes

$$\frac{A - A_0}{NkT} = -\frac{\kappa^4}{64\pi^2\rho}\int \frac{g_0(12)}{r_{12}^2}\,d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int \frac{g_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots . \qquad (6.15)$$

Each integral in (6.16) is divergent because of the long range of the Coulomb potential. To get anything useful we must sum these divergent terms.

It is convenient to rewrite Eq. (6.15) as

$$\begin{aligned}\frac{A - A_0}{NkT} = &-\frac{\kappa^4}{64\pi^2\rho}\int \frac{d\underset{\sim}{r}_2}{r_{12}^2} + \frac{\kappa^6}{384\pi^3\rho}\int \frac{d\underset{\sim}{r}_2 d\underset{\sim}{r}_3}{r_{12}r_{13}r_{23}} + \cdots \\ &+ \frac{\kappa^6}{128\pi^3\rho}\int \frac{h_0(12)\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3}{r_{12}r_{13}r_{23}} + \cdots \qquad (6.16) \\ &- \frac{\kappa^4}{64\pi^2\rho}\int \frac{h_0(12)}{r_{12}^2}\,d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int \frac{h_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots .\end{aligned}$$

Each of the members of the first sequence of terms is divergent, as is each member of the second sequence. Only the members of the last sequence of terms, involving $h_0(12) = g_0(12) - 1$ and

$$h_0(123) = g_0(123) - 1 - h_0(12) - h_0(13) - h_0(23) \quad , \qquad (6.17)$$

are convergent. All of the integrations are outside the cores (i.e., $r_{ij} \geq \sigma$). However, to evaluate the sum of the first sequence, let us extend the range of integration to include all $r_{ij} \geq 0$. No error is introduced since we have merely added and subtracted the regions $0 \leq r_{ij} \leq \sigma$.

Rather than deal with Eq. (6.16), it is simpler to obtain the sum of the first sequence of terms by considering the corresponding expansion of $g_{ij}(r)$, i.e.,

$$\begin{aligned}g_{ij}(r_{12}) = 1 &- \frac{\beta z_i z_j e^2}{\varepsilon}\left\{\frac{1}{r_{12}} - \frac{\kappa^2}{4\pi}\int \frac{d\underset{\sim}{r}_3}{r_{13}r_{23}} + \cdots\right\} \\ &+ \frac{\beta^2 z_i^2 z_j^2 e^4}{2\varepsilon^2 r_{12}^2} + \cdots + \frac{\beta z_i z_j e^2}{\varepsilon}\, h_0(r_{12})\,\frac{\kappa^2}{4\pi}\int \frac{d\underset{\sim}{r}_3}{r_{13}r_{23}} \\ &+ \frac{2\beta z_i z_j e^2}{\varepsilon}\,\frac{\kappa^2}{4\pi}\int \frac{h_0(13)}{r_{13}r_{23}}\,d\underset{\sim}{r}_3 + \cdots + h_0(r_{12}) - \frac{\beta z_i z_j e^2}{\varepsilon r_{12}}\, h_0(12)\end{aligned}$$

$$+ \frac{\beta z_i^2 z_j^2 e^4}{2\varepsilon^2 r_{12}^2} h_0(12) + \dots + \frac{\beta z_i z_j e^2}{\varepsilon} \frac{\kappa^2}{4\pi} \int \frac{h_0(123)}{r_{13} r_{23}} d\underset{\sim}{r}_3$$

$$+ \dots \quad . \tag{6.18}$$

Again we can assume without loss of generality that Eq. (6.18) is valid for all $r_{ij} \leq 0$. The sequence of terms in the curly brackets is called a ring or chain sum since their terms in this sequence are simple ring diagrams consisting of repeated convolutions of $1/r_{ij}$.

Thus, defining the ring or chain sum,

$$C_{ij}(r_{12}) = \frac{\beta z_i z_j e^2}{\varepsilon} \left\{ \frac{1}{r_{12}} - \frac{\kappa^2}{4\pi} \int \frac{d\underset{\sim}{r}_3}{r_{13} r_{23}} + \dots \right\} , \tag{6.19}$$

and taking the Fourier transform,

$$\hat{C}_{ij}(k) = \frac{4\pi}{k} \int_0^\infty r C_{ij}(r) \sin kr dr, \tag{6.20}$$

we have

$$\hat{C}_{ij}(k) = \frac{4\pi\beta z_i z_j e^2}{\varepsilon k^2} \left\{ 1 - \frac{\kappa^2}{k^2} + \frac{\kappa^4}{k^4} + \dots \right\}$$

$$= \frac{4\pi\beta z_i z_j}{\varepsilon} \frac{1}{k^2 + \kappa^2} . \tag{6.21}$$

Hence,

$$C_{ij}(r) = \frac{\beta z_i z_j e^2}{\varepsilon} \frac{e^{-\kappa r}}{r} \quad (r \geq 0) . \tag{6.22}$$

Keeping only the first two terms in Eq. (6.18) we have the Debye-Hückel approximation

$$g_{ij}(r) = 1 - C_{ij}(r) . \tag{6.23}$$

Equation (6.23) is identical to Eq. (6.8). From Eq. (6.23) we obtain

$$E_i/NkT = - \frac{\kappa^3}{8\pi\rho} . \tag{6.24}$$

Hence,

$$\frac{A - A_0}{NkT} = - \frac{\kappa^3}{12\pi\rho} . \tag{6.25}$$

Thus, Eq. (6.16) becomes

$$\frac{A-A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{64\pi^2\rho}\int \frac{h_0(12)}{r_{12}^2}\, d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int \frac{h_0(123)}{r_{12}r_{13}r_{23}}\, d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \frac{\kappa^6}{128\pi^3\rho}\int \frac{h_0(12)}{r_{12}r_{13}r_{23}}\, d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots \quad . \tag{6.26}$$

Note that as a result of the resummation, the free energy is not an analytic function of β and ρ but is an analytic function of $\beta^{\frac{1}{2}}$ and $\rho^{\frac{1}{2}}$. We must still resum the last sequence (which contains divergent terms). We do this by techniques similar to those used to obtain Eq. (6.22). The result is

$$\frac{A-A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{64\pi^2\rho}\int \frac{h_0(12)}{r_{12}^2}\, e^{-2\kappa r_{12}} d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int \frac{h_0(123)}{r_{12}r_{13}r_{23}}\, d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots , \tag{6.27}$$

which may be expanded into the Stell-Lebowitz$^{(11)}$ series

$$\frac{A-A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{64\pi^2\rho}\int \frac{h_0(12)}{r_{12}^2}\, d\underset{\sim}{r}_2 + \frac{\kappa^5}{32\pi^2\rho}\int \frac{h_0(12)}{r}\, d\underset{\sim}{r}_2 - \frac{\kappa^6}{32\pi^2\rho}\left\{\int h_0(12)\, d\underset{\sim}{r}_2 - \frac{1}{12\pi}\int \frac{h_0(123)}{r_{12}r_{13}r_{23}}\, d\underset{\sim}{r}_2 d\underset{\sim}{r}_3\right\} + \cdots . \tag{6.28}$$

This series converges very slowly. The sum of the series may be approximated by a Padé approximant. The results$^{(12)}$ are very similar to the mean spherical approximation results, obtained from Eqs. (6.9) to (6.12).

We have derived the Stell-Lebowitz expansion from perturbation theory. Stell and Lebowitz did not use this method but obtained their series in a more direct manner. Although the method given here is less direct, it does indicate how improvements may be made.

The integrations in Eq. (6.28) are over all space ($r_{ij} \geq 0$). This is natural in the Stell-Lebowitz derivation. However, in our original perturbation expansion, the integrations are over $r_{ij} \geq \sigma$. This suggests that improved results might be obtained by taking the integrals for the regions $0 \leq r_{ij} \leq \sigma$ and combining them with the κ^3 term. Thus

$$\frac{A - A_0}{NkT} = - \frac{\kappa^3}{12\pi\rho} \left[1 - \frac{3}{4}\sigma + \frac{3}{4}\kappa\sigma - \frac{7}{8}\kappa^3\sigma^3 + \cdots\right] + \cdots \quad . \tag{6.29}$$

At first sight $\kappa^3(1 - 3\kappa\sigma/4 + 3\kappa^2\sigma^2/4 - 7\kappa^3\sigma^3/8 + \cdots)$ seems like an unpromising combination; it is, in fact, $(2\Gamma)^3(1 + 3\Gamma\sigma/2)$. Thus

$$\frac{A - A_0}{NkT} = - \frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} - \frac{\kappa^4}{16\pi\rho}\int_0^\infty h_0(r)dr + \cdots . \tag{6.30}$$

Retaining only the first term gives the mean spherical approximation.

The corresponding result for $g_{ij}(r)$ is

$$g_{ij}(r) = g_0(r) - C^{MSA}_{ij}(r) - \frac{\beta z_i z_j e^2}{\varepsilon r} h_0(r) + \cdots \quad (r > \sigma), \tag{6.31}$$

where

$$C^{MSA}_{ij} = \frac{\beta z_i z_j e^2}{\varepsilon(1 + \Gamma\sigma)^2} \frac{f(r - \sigma)}{r} \quad . \tag{6.32}$$

Again, truncation of (6.31) after $C^{MSA}_{ij}(r)$ gives the mean spherical approximation. The optimized random phase approximation of Anderson et al.(13) consists of truncation of Eq. (6.31) after $C^{MSA}_{ij}(r)$ and so is equivalent to the mean spherical approximation.

The series of corrections to the mean spherical approximation still converges slowly and must be summed by Padé methods. There must be extensive cancellation among the terms as the Padé results are not much different from the mean spherical approximation results.

Henderson and Blum(14) have suggested changing the expansion parameter from κ to 2Γ. Thus,

$$\frac{A - A_0}{NkT} = - \frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} - \frac{(2\Gamma)^4}{16\pi\rho}\int_\sigma^\infty h_0(r)\,dr + \cdots \quad . \tag{6.33}$$

The higher-order terms in this expansion are given by Henderson and Blum. Since $2\Gamma \leq \kappa$ this series of corrections to the mean spherical approximation is better behaved. In fact, at normal electrolyte concentrations the corrections are negligible.

At low concentrations, the correction terms, given in Eqs. (6.30) and (6.33) are not the most important corrections to the mean spherical approximation result. This is because, there is, in the fourth-order term [see Eq. (4.12)], the contribution

$$\frac{\Delta A}{NkT} = -\frac{1}{48}\beta^4\rho\sum_{ij}x_i x_j\int u_{ij}^4(r)g_0(r)d\underset{\sim}{r} \ . \tag{6.34}$$

Contributions analogous to this appear in every even-order perturbation term. The corresponding terms in the odd-order perturbation terms do not contribute because of charge neutrality.

The integral in Eq. (6.34) converges because r^{-4} goes to zero sufficiently fast to prevent a divergence. However, since the mean spherical approximation works well at higher densities, the contribution of this β^4 term must disappear at these higher densities due to some cancellation with terms which are higher-order in the density. Hence, even though a resummation is not forced upon us to prevent a divergence, a resummation is desirable as it approximates this cancellation. The effect of the resummation is to replace

$$\beta u_1(r) = \frac{\beta z_i z_j e^2}{\varepsilon r} \tag{6.35}$$

by $C_{ij}(r)$. Thus, we have led to the approximate correction term

$$\frac{\Delta A}{NkT} = -\frac{1}{2}\rho\sum_{ij}x_i x_j\int\sum_{n=2}^{\infty}\left\{\frac{1}{(2n)!}[C_{ij}^{MSA}(12)]^{2n}g_0(12)d\underset{\sim}{r}_2\right\} . \tag{6.36}$$

We could add ΔA given by (6.36) to (6.30) or (6.33) with all the known terms, that is, the integrals (6.28) with the integration region $r_{ij} \geq \sigma$. Andersen et al.$^{(13)}$ keep only the κ^4 term in (6.30) and replace $\beta^2 u_1^2(r)$ in this term by $C_{ij}^2(r)$ to obtain what they call the ORPA+B$_2$ approximation. In this approximation

$$\begin{aligned}\frac{A - A_0}{NkT} = &-\frac{(2\Gamma)^3(1+3\Gamma\sigma/2)}{12\pi\rho}\\ &-\frac{1}{4}\rho\sum_{ij}x_i x_j\int h_0(12)[C_{ij}^{MSA}(12)]^2 d\underset{\sim}{r}_2\\ &-\frac{1}{2}\rho\sum_{ij}x_i x_j\int g_0(12)\sum_{n=2}^{\infty}\frac{1}{(2n)!}[C_{ij}^{MSA}(12)]^{2n}d\underset{\sim}{r}_2,\end{aligned} \tag{6.37}$$

which becomes

$$\frac{A - A_0}{NkT} = -\frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} - \frac{(2\Gamma)^4}{64\pi^2\rho}\int \frac{h_0(r)}{r^2} f^2(r - \sigma)d\underset{\sim}{r}$$
$$-\frac{1}{2}\rho\sum_{n=2}^{\infty}\frac{1}{(2n)!}\left[\frac{\beta z^2e^2}{\varepsilon(1 + \Gamma\sigma)^2}\right]^{2n}\int\frac{g_0(r)}{r^{2n}} f^{2n}(r - \sigma)d\underset{\sim}{r} , \quad (6.38)$$

where the integrations are over the region $r \geqq \sigma$. The results of this approximation are shown in Figs. 7 and 8. They are an improvement over the mean spherical approximation results and are comparable to those of the hypernetted chain approximation.

In addition to the theories of electrolytes outlined above, there is another theory of electrolytes which as been useful. It is the modified Poisson-Boltzmann approximation. We do not have time or space to outline this approach here. We have limited ourselves to theories based upon either the Ornstein-Zernike equation or perturbation theory. The modified Poisson-Boltzmann approximation and other approximations have been admirably reviewed by Outhwaite(15).

The theories outlined above provide reasonably good descriptions of the model ionic fluid defined by Eq. (6.1). The main deficiency is the nonmolecular model of the solvent which appears only through the dielectric constant ε. What is needed is a more realistic treatment of the solvent.

7. APPLICATION TO MOLECULAR FLUIDS

Molecular fluids, in which the intermolecular potential depends on orientation as well as position, can be treated by fairly straightforward extensions of the methods discussed above.

First let us consider integral equation approaches. It is sometimes helpful to expand the pair-potential and the correlation functions using an orthogonal basis set. Restricting ourselves for simplicity to molecules with cylindrical symmetry, we have

$$u(1,2) = u^{000}(r) + u^{110}(r)\phi^{110} + u^{112}(r)\phi^{112} + \cdots, \quad (7.1)$$

etc., where the coefficients are obtained as projections,

$$u^{mnl}(r) = \frac{\int u(1,2)\phi^{mnl}(\Omega_1,\Omega_2)d\Omega_1 d\Omega_2}{\int [\phi^{mnl}(\Omega_1,\Omega_2)]^2 d\Omega_1 d\Omega_2} \quad . \tag{7.2}$$

The first two ϕ^{mnl} (after $\phi^{000} = 1$) are

$$\phi^{110} = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \quad , \tag{7.3}$$

$$\phi^{112} = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \quad , \tag{7.4}$$

where θ_i, ϕ_i are the polar angles of molecule i.

Coupling some approximation with the Ornstein-Zernike equation, Eq. (3.11), gives an approximate integral equation. The simplest is the mean spherical approximation, where

$$c(1,2) = -\beta u(1,2), \tag{7.5}$$

outside the hard core, and

$$h(1,2) = -1 \quad , \tag{7.6}$$

inside the hard core. Because of the linear relation between c(1,2) and u(1,2) in Eq. (7.5) a truncated series for u(1,2) with a limited number of $u^{mnl}(r)$ will produce a similarly truncated series for c(1,2) and h(1,2).

A nonlinear approximation, such as the hypernetted chain approximation, would produce an infinite series for h(1,2) and c(1,2) even if the series for u(1,2) contained a small number of terms. An approximation, based upon the hypernetted chain approximation, which does limit the number of terms in the h(1,2) and c(1,2) expansions is obtained by truncating the expansion of the logarithm in the hypernetted chain approximation,

$$\ln g(1,2) + \beta u(1,2) = h(1,2) - c(1,2) \quad , \tag{7.7}$$

to first order. Thus,

$$c^{000}(r) = h^{000}(r) - \ln [1 + h^{000}(r)] - \beta u^{000}(r) \tag{7.8}$$

and

$$c^{mnl}(r) = \frac{h^{000}(r)}{1 + h^{000}(r)} h^{mnl}(r) - \beta u^{mnl}(r), \tag{7.9}$$

for m, n, l not all equal to zero. Equations (7.8) and (7.9) are called the linearized hypernetted chain approximation(16). Although this is a linearized version of the hypernetted chain approximation, it is different from the mean spherical approximation. The linearized hypernetted approximation reduces to the mean spherical approximation if

$$h^{000}(r) \cong 1. \tag{7.10}$$

Gaylor et al.(197) have proposed an alternative linearized hypernetted chain approximation which is an improvement at low densities, at least. An improved approximation, called the quadratic hypernetted chain approximation follows if the logarithm in Eq. (7.7) is expanded to second order.

Other integral equations can be formulated. Cummings et al.(18) have considered some of these and obtained numerical results for short-ranged anisotropic potentials. Here we will limit ourselves to the relative simple dipolar hard-sphere potential,

$$u(1,2) = u_{HS}(r) - \frac{\mu^2}{r_{12}^3} D(1,2), \tag{2.30}$$

where μ is the dipole moment of a molecule and

$$D(1,2) = \phi^{112} \tag{7.11}$$

is given by (2.31) or (7.4), and the mean spherical and linearized hypernetted chain approximations. The dipolar hard-sphere potential is simple not only because of the limited basis set but also because the potential core is spherical.

Wertheim(19) has obtained an analytic solution for the dipolar hard-sphere potential using the mean spherical approximation. Following his notation, he finds

$$h(1,2) = h_s(r_{12}) + h_D(r_{12})D(1,2) + h_\Delta(r_{12})\Delta(1,2), \tag{7.12}$$

where

$$h_s(r) = h^{000}(r), \tag{7.13}$$

$$h_D(r) = h^{112}(r), \tag{7.14}$$

$$h_\Delta(r) = h^{110}(r), \tag{7.15}$$

D(1,2) is given by Eq. (7.11), and

$$\begin{aligned}\Delta(1,2) &= \hat{\mu}_1 \cdot \hat{\mu}_2 \\ &= \phi^{110}.\end{aligned} \tag{7.16}$$

We note that

$$\int D(1,2)\,d\Omega_1 d\Omega_2 = \int \Delta(1,2)\,d\Omega_1 d\Omega_i = 0, \tag{7.17}$$

$$\int D^2(1,2)\,d\Omega_1 d\Omega_2 = \frac{2}{3}, \tag{7.18}$$

$$\int \Delta^2(1,2)\,d\Omega_1 d\Omega_2 = \frac{1}{3}, \tag{7.19}$$

and that D(1,2) and $\Delta(1,2)$ are orthogonal, i.e.,

$$\int D(1,2)\Delta(1,2)\,d\Omega_1 d\Omega_2 = 0 \tag{7.20}$$

Wertheim found that $h_s(r)$ is just the Percus-Yevick/mean spherical approximation result for hard-spheres which can be obtained from Eq. (3.28). Further, he found that if κ is defined by

$$\xi = \kappa\eta, \tag{7.21}$$

where $\eta = \pi^2\rho\sigma^3/6$ and ξ is obtained from

$$\begin{aligned} y &= \frac{4\pi\beta\mu^2\rho}{9} \\ &= \frac{1}{3}\,[q(2\xi) - q(-\xi)], \end{aligned} \tag{7.22}$$

where

$$q(x) = \frac{(1+2x)^2}{(1-x)^4}, \tag{7.23}$$

then

$$h_{\Delta}(r) = \begin{cases} 0 & (r < \sigma), \\ 2\kappa[h_{s}(r, 2\kappa\rho) - h_{s}(r, -k\rho)] & (r > \sigma), \end{cases} \tag{7.24}$$

and

$$h_{D}(r) = \begin{cases} 0 & (r < \sigma), \\ \hat{h}_{D}(r) - \frac{3}{r^{3}} \int_{0}^{r} \hat{h}_{D}(s) s^{2} ds & (r > \sigma), \end{cases} \tag{7.25}$$

where

$$\hat{h}_{D}(r) = \kappa[2h_{s}(r, 2\kappa\rho) + h_{s}(r, -\kappa\rho)]. \tag{7.26}$$

The apparently mysterious equations for κ can also be written as

$$\kappa = \int_{\sigma}^{\infty} \frac{h_{D}(r)}{r} \, dr. \tag{7.27}$$

The thermodynamic functions can be calculated from

$$\frac{p}{\rho kT} = 1 + 4\eta y_{s}(\sigma) - \frac{1}{3} \beta\rho\mu^{2} \int \frac{h_{D}(r)}{r^{3}} \, d\underset{\sim}{r} \ , \tag{7.28}$$

$$kT \frac{\partial\rho}{\partial p} = 1 + \rho \int h_{s}(r) d\underset{\sim}{r} \ , \tag{7.29}$$

or

$$E_{i} = -\frac{1}{3} N\rho\mu^{2} \int \frac{h_{D}(r)}{r^{3}} \, d\underset{\sim}{r} \ . \tag{7.30}$$

Equation (7.30) gives by far the most reliable results.

The dielectric constant ε is calculated from

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = y g_{k} \ , \tag{7.31}$$

where

$$y = \frac{4\pi}{9} \beta\rho\mu^{2} \tag{7.32}$$

and

$$g_{k} = 1 + \frac{1}{3} \rho \int h_{\Delta}(r) \, d\underset{\sim}{r} \ . \tag{7.33}$$

It is interesting to note that Onsager's approximation for ε is obtained from Eq. (7.31) by putting $g_k = 1$. In the mean spherical approximation

$$\varepsilon = \frac{(1+4\xi)^2 (1+\xi)^4}{(1-2\xi)^6} . \qquad (7.34)$$

The mean spherical approximation pair distribution function for dipolar hard-spheres is compared with computer simulation results(20,21) shown in Fig. 9. The mean spherical approximation gives fairly good results for $h_s(r)$. Furhter we see that the simulation $h_s(r)$ for dipolar hard-spheres is very nearly equal to that for hard spheres but is somewhat larger. The mean spherical approximation for $h_D(r)$ and $h_\Delta(r)$ are rather poor. Interestingly, the approximations

$$h_D(r) = g_s(r) h_D^{MSA}(r) \qquad (7.35)$$

$$h_\Delta(r) = g_s(r) h_\Delta^{MSA}(r) \qquad (7.36)$$

are much better.

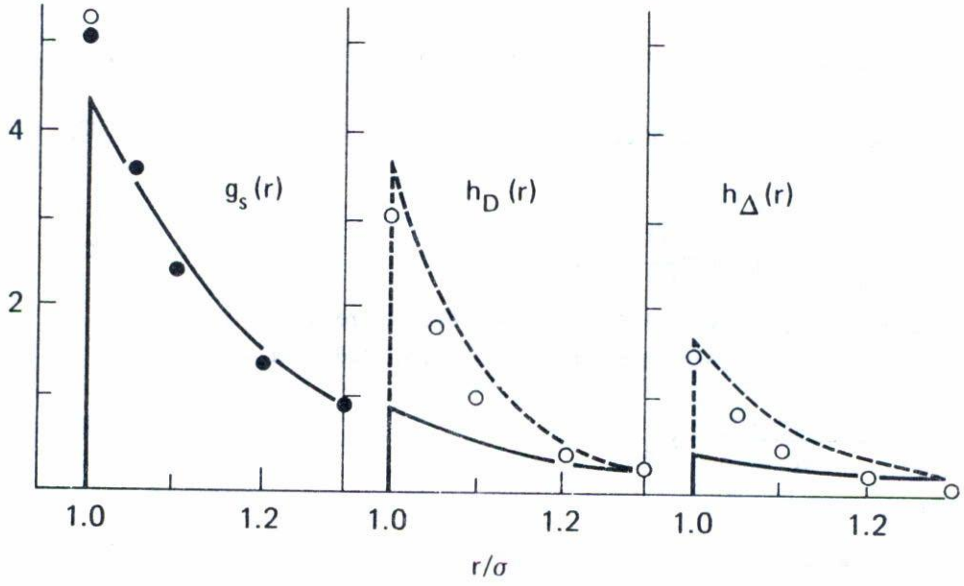

Fig. 9. Pair distribution functions for the dipolar hard-sphere fluid at $\rho\sigma^3 = 0.9$. The points given by ● and o give the computer simulation results for $\beta\mu^2 = 0$ (hard-spheres) and $\beta\mu^2 = 1$, respectively. The solid and broken curves give the results of the MSA and Eqs. (7.35) and (7.36), respectively, for $\beta\mu^2 = 1$.

The mean spherical approximation free energy and dielectric constant for dipolar hard-spheres are plotted in Figs. 10 and 11. The results are fairly reasonable. The mean spherical approximation dielectric constant is much more satisfactory than the Clausius-Mossotti result,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = y , \tag{7.37}$$

and the Onsager result,

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = y . \tag{7.38}$$

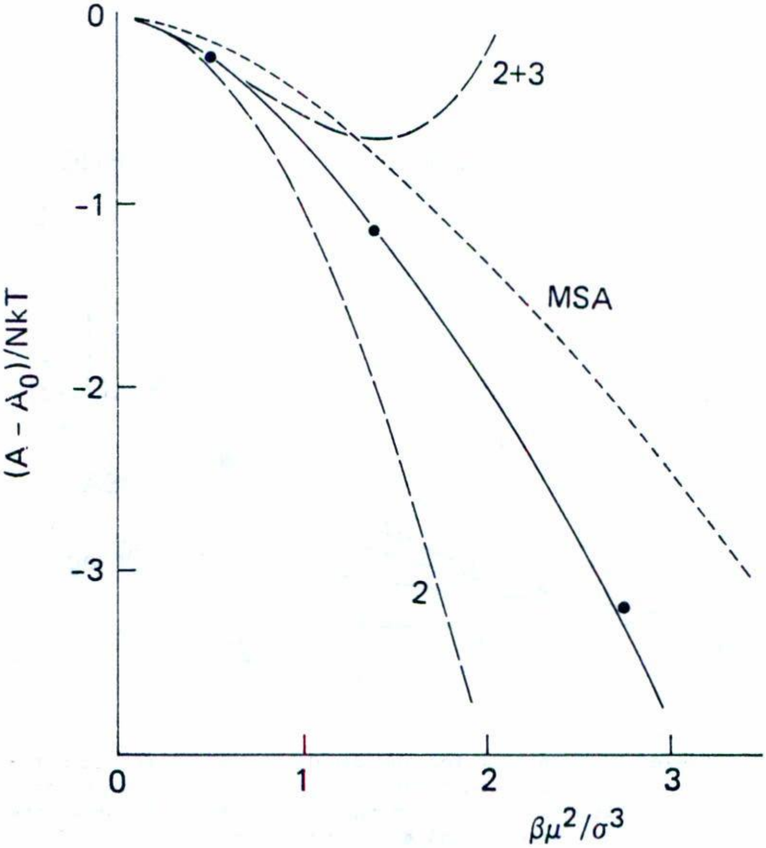

Fig. 10. Free energy of the dipolar hard-sphere fluid ($\rho\sigma^3 = 0.8344$) as a function of reduced dipole moment. The points are the simulation values of Patey and Valleau. The broken curves marked 2 and 2+3 give the results of Eq. (7.39) when truncated after 2 and 3 terms, respectively. The solid curves give the results of Eq. (7.47) and the curved marked MSA gives the results of the mean spherical approximation.

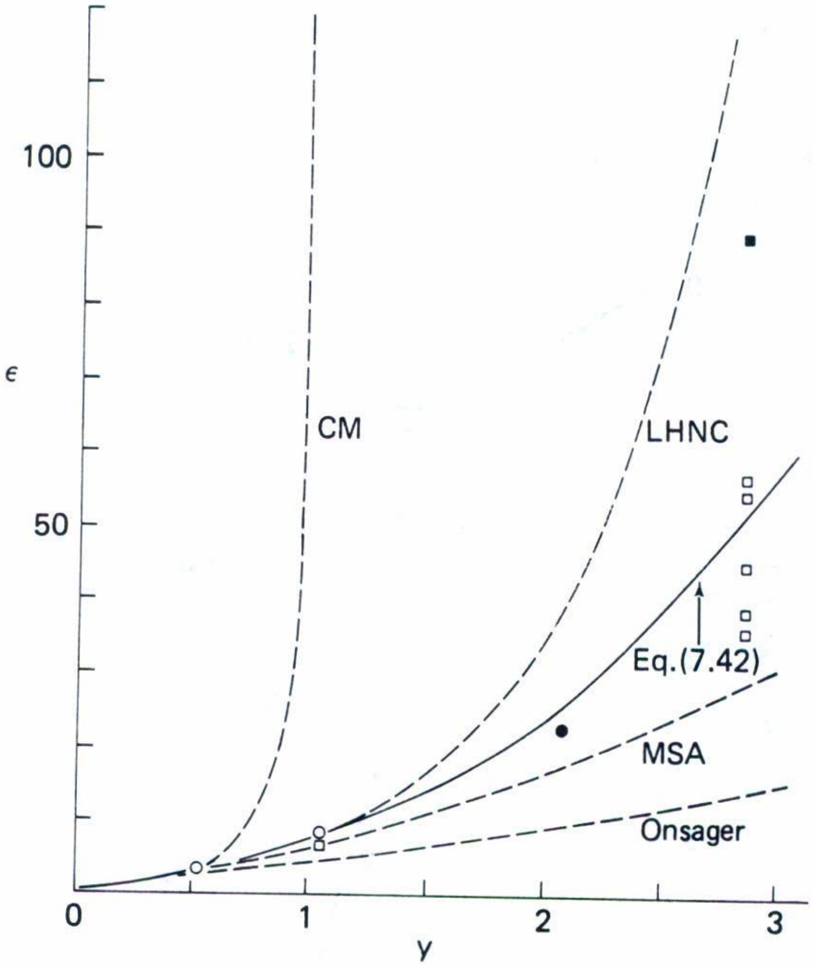

Fig. 11. Dielectric constant for the dipolar hard-sphere fluid for $\rho^* = 0.8$. The solid curve gives the perturbation theory results and the broken curves give the results for some other theories. The points marked ○ and ● are simulation estimates of Levesque et al. and DeLeeuw et al., respectively. The points marked □ and ■ are, respectively, simulation estimates obtained by Adams using an Ewald-Kornfeld summation and an extrapolation to zero field of the computed values of the polarization in the direction of an applied field.

Perturbation theory can also be applied to the dipolar hard sphere system. The first-order term vanishes because of Eq. (7.17). Similarly, only the first integral in the second-order term is nonzero and only the ring diagram in the third order is nonvanishing. After performing the angular integrations,

$$A = A_0 + \beta^2\mu^4 A_2 + \beta^3\mu^6 A_3 + \cdots, \tag{7.39}$$

where

$$\frac{A_2}{NkT} = -\frac{1}{6}\rho\int\frac{g_0(r)}{r^6}\,dr \tag{7.40}$$

and

$$\frac{A_3}{NkT} = -\frac{1}{54}\rho^2 I_{ddd}. \tag{7.41}$$

Similarly, the perturbation expansion for ε is

$$\varepsilon = 1 + 3y + 3y^2 + 3y^3\left(\frac{9I_{dd\Delta}}{16\pi^2} - 1\right) + \cdots . \tag{7.42}$$

In Eqs. (7.41) and (7.42)

$$I_{ddd} = \int\frac{1 + 3\cos\theta_1\cos\theta_2\cos\theta_3}{r_{12}^3 r_{13}^3 r_{23}^3}\, g_0(123)\,d\underset{\sim}{r}_2\,d\underset{\sim}{r}_3 \tag{7.43}$$

and

$$I_{dd\Delta} = \int\frac{3\cos^3\theta_3 - 1}{r_{13}^3 r_{13}^3}\, g_0(123)\,d\underset{\sim}{r}_2\,d\underset{\sim}{r}_3 . \tag{7.44}$$

Barker et al.(22) and, more recently, Tani et al.(23) have calculated I_{ddd} and Tani et al.(23) have calculated $I_{dd\Delta}$. A numerical fit of their results is given by

$$I_{ddd} = \frac{5\pi^2}{3}\sigma^6\,\frac{1 + 1.12754\rho\sigma^3 + 0.56192\rho^2\sigma^6}{1 - 0.05495\rho\sigma^3 + 0.13332\rho^2\sigma^6} \tag{7.45}$$

and

$$I_{dd\Delta} = \frac{17\pi^2}{9}\sigma^6\,\frac{1 - 0.93952\rho\sigma^3 + 0.36714\rho^2\sigma^6}{1 - 0.92398\rho\sigma^3 + 0.23323\rho^2\sigma^6} . \tag{7.46}$$

The free energy calculated from Eq. (7.39) with A_0 and A_2 and A_3 included is plotted in Fig. 10. The series converges poorly. However, Rushbrooke et al.$^{(24)}$ have found that the Padé sum,

$$A = A_0 + \beta^2\mu^4 \frac{A_2}{1 - \beta\mu^2 A_3/A_2} , \tag{7.47}$$

is in good agreement with computer simulations$^{(25)}$. On the other hand, the perturbation series for the dielectric constant seems to converge and, as is seen in Fig. 11, good agreement with computer simulation results$^{(26)}$ is obtained from Eq. (7.42).

We have seen for the case of charged hard-sphere, it is helpful to remove the mean spherical approximation results from the perturbation series and write the series as a correction to the mean spherical approximation. This can also be done for dipolar hard-spheres. The results is

$$A = A_{\text{MSA}} + \beta^2\mu^4 A_2' + \beta^3\mu^6 A_3' + \cdots , \tag{7.48}$$

where

$$\frac{A_2'}{NkT} = -\frac{1}{6}\rho\int \frac{h_0(r)}{r^6}\, d\underset{\sim}{r} \tag{7.49}$$

and

$$\frac{A_3'}{NkT} = -\frac{1}{54}\rho^2\left(I_{\text{ddd}} - \frac{5\pi^6}{3}\sigma^6\right). \tag{7.50}$$

The free energy calculated from Eq. (7.48) with A_{MSA}, A_2', and A_3' included is plotted in Fig. 12. The series in Eq. (7.48) converges better than that in Eq. (7.39). However, good agreement with simulation results$^{(26)}$ is obtained only if the Padé series,

$$A = A_{\text{MSA}} + \beta^2\mu^4 \frac{A_2'}{1 - \beta\mu^2\, A_3'/A_2'} , \tag{7.51}$$

is used.

The corresponding result for the dielectric constant is

$$\varepsilon = \varepsilon_{\mathrm{MSA}} + 3y^3 \left[\frac{9I_{dd\Delta}}{16\pi^2} - \frac{17}{16}\right] \qquad (7.52)$$

The results of Eq. (7.52) are nearly identical to those of Eq. (7.42) in Fig. 11.

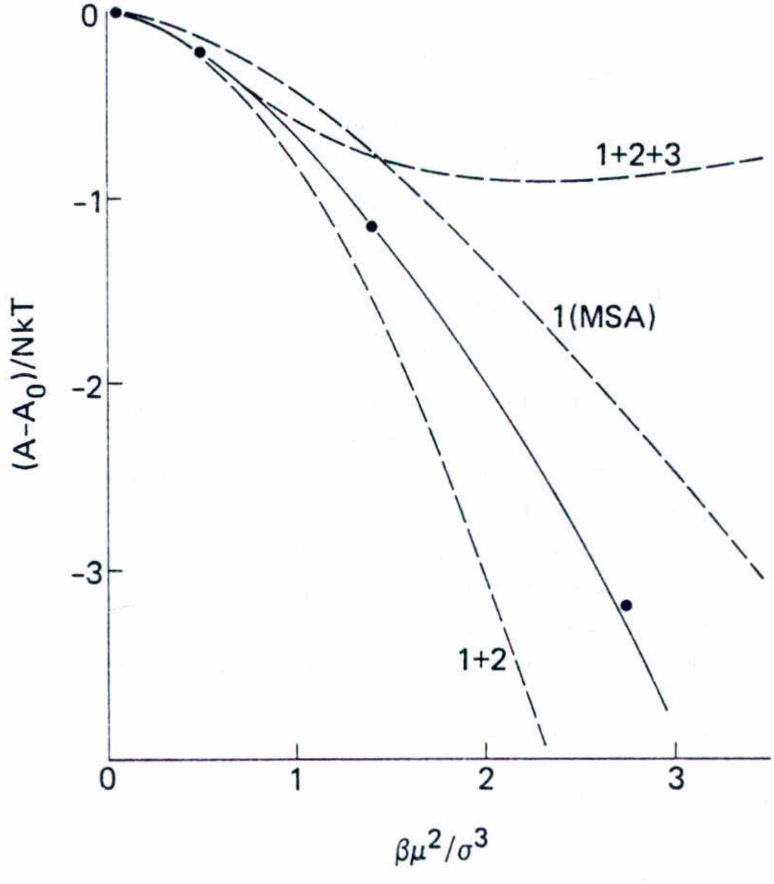

Fig. 12. Free energy of the dipolar hard-sphere ($\rho\sigma^3 = 0.8344$) as a function of reduced dipole moment. The points have the same meaning as in Fig. 10. The broken curves marked 1, 1+2, 1+2+3 give the results of Eq. (7.48) when truncated after 1, 2, and 3 terms, respectively. The solid curve gives the results of Eq. (7.51).

Equations (7.47) and (7.51) will be inadequate at low densities because of the neglect of the two-fourth and higher-order terms. For example, we could generalize Eq. (7.47) to

$$\begin{aligned}\frac{A - A_0}{NkT} &= \beta^2\mu^4 \frac{A_2/NkT}{1-\beta\mu^2\dfrac{A_3}{A_2}} - \frac{1}{6}\,\rho\int h_0(r)h_D^2(r)d\mathbf{r} \\ &\quad - \frac{1}{2}\,\rho\sum_{n=2}^{\infty}\frac{1}{(2n)!}\int g_0(r)h_D^{2n}(r)d\mathbf{r}\int D^{2n}(1,2)d\Omega_1 d\Omega_2 \\ &= \beta^2\mu^4 \frac{A_2/NkT}{1-\beta\mu^2\dfrac{A_3}{A_2}} - \frac{1}{6}\,\rho\int h_0(r)h_D^2(r)d\mathbf{r} \\ &\quad - \frac{1}{2}\,\rho\sum_{n=2}^{\infty} K_{2n}\int g_0(r)h_D^{2n}(r)dr\ ,\end{aligned} \tag{7.53}$$

where

$$K_n = 2^n\left[\frac{n!}{(2n+1)!}\right]^2\sum_{i=0}^{n}\frac{(2i)!}{(i!)^2}\quad . \tag{7.54}$$

The perturbation theory considered above is upon a u-expansion. A perturbation theory based upon an f-expansion is also possible and has some advantages.$^{(27)}$ It does have the disadvantage that the angular integrals cannot be evaluated analytically.

In Section 6 we consider a system of charged hard-spheres and in this section we considered the dipolar hard-sphere system. It is tempting to consider a charged hard-sphere/dipolar hard-sphere mixture as a more realistic model of an electrolyte. For this system the interactions are

$$u_{ij}(r) = u_{HS}(r) + \frac{z_i z_j e^2}{r} \tag{7.55}$$

for ion-ion interactions,

$$u_{ij}(r) = u_{HS}(r) + \frac{z_i e\mu}{r^2}\,(\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\mu}}_j) \tag{7.56}$$

for ion-dipole interactions, and

$$u_{ij}(r) = u_{HS}(r) - \frac{\mu^2}{r^3}\,D(1,2) \tag{7.57}$$

for the dipole-dipole interactions. Note that ε no longer appears in the denominator of the Coulomb interaction.

The mean spherical approximation has been applied to this system$^{(28)}$. The results are complex and beyond the scope of these lectures Perturbation theory can also be applied$^{(29)}$ to this system. Again the results are complex. However, a few comments are of value. If all the hard-spheres have the same diameter, the first-order terms vanish because of charge neutrality or angle interactions. In second and third order only the terms involving u^2_{12} or $u_{12}u_{13}u_{23}$ survive. Thus,

$$\frac{A-A_0}{NkT} = -\frac{1}{4}\,\rho\beta^2\sum_{ij} x_i x_j \int d\underset{\sim}{r}_2 \int u^2_{ij}(r_{12})\,d\Omega_1 d\Omega_2$$

$$+\frac{1}{6}\,\rho^2\beta^3\sum_{ijk} x_i x_j x_k \int d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 \int u_{ij}(12)u_{jk}(23)u_{ij}(13)\,d\Omega_1 d\Omega_2 d\Omega_3 \;. \tag{7.58}$$

Many of these integrals diverge. Thus, ring or chain summations must be performed. These summations are complex and beyond our scope. However, it is instructive to calculate the ring sum for the ion-ion interactions. Defining

$$C_{ij}(12) = \beta u_{ij}(12) - \beta^2\rho\sum_k \int u_{ik}(13)u_{kj}(23)\,d\underset{\sim}{r}_3 d\Omega_3 + \cdots \;. \tag{7.59}$$

For the ion-ion interaction

$$C_{ij}(r_{12}) = \frac{\beta z_i z_j e^2}{r_{12}} - \beta^2\, z_i z_j e^4 \sum_{k=1}^{2} z_k^2 \rho k \int \frac{d\underset{\sim}{r}_3}{r_{13}r_{23}}$$

$$-\,\beta^2 z_i z_j e^2\mu^2\rho_d \frac{1}{3}\int \frac{\cos\theta_3}{r^2_{13}r^2_{23}}\,d\underset{\sim}{r}_3 + \cdots , \tag{7.60}$$

where species 1 and 2 have been assumed to be the charged hard-spheres, species 3 is assumed to be dipolar hard-sphere, and ρ_d is the density of the dipolar hard-spheres. Now using Eq. (3.14) and

$$\cos\theta_3 = \frac{r^2_{13} + r^2_{23} - r^2_{12}}{2r_{13}r_{23}} \quad , \tag{7.61}$$

we obtain

$$\int \frac{\cos\theta_3}{r^2_{13}r^2_{23}}\,d\underset{\sim}{r}_3 = \frac{4\pi}{r_{12}} \tag{7.62}$$

and, thus,

$$C_{ij}(r_{12}) = \beta z_i z_j e^2 \left[\frac{1}{r_{12}}(1-3y) - \frac{\kappa_0^2}{4\pi}\int \frac{d\underset{\sim}{r}_3}{r_{13}r_{23}} + \cdots\right], \tag{7.63}$$

where

$$\kappa_0^2 = 4\pi\beta e^2 \sum_k z_k^2 \rho_k \tag{7.64}$$

and

$$y = \frac{4\pi}{9}\beta\mu^2\rho_d \quad . \tag{7.65}$$

Proceeding a before,

$$C_{ij} = \frac{\beta z_i z_j e^2}{\varepsilon}\;\frac{e^{-\kappa r_{12}}}{r_{12}}, \tag{7.66}$$

where $\kappa = \kappa_0\sqrt{\varepsilon}$ and

$$1/\varepsilon = 1-3y + \cdots \tag{7.67}$$

is the inverse of the dielectric constant. Hence, even though the direct. Coulomb interaction does not contain the dielectric constant, the chain sum which includes the screening and solvent interaction does contain ε.

The contents of this section give only and introduction to the theory of molecular fluids. For further applications, especially to fluids with nonspherical cores, the forthcoming book of Gray and Gubbins$^{(30)}$ is recommended.

8. APPLICATION TO ELECTRIFIED INTERFACES (THE DOUBLE LAYER)

We consider an electrolyte near a charged electrode. As before, we consider the ions to be charged hard-spheres of diameter σ. The electrode is approximated as a uniform hard charged wall. First consider the case where the solvent is a uniform dielectric medium whose dielectric constant is ε.

If the electrode is charged, there will be an accumulation near the electrode of ions whose charge is opposite to that of the electrode.

We can then speak of a double layer of charge.

The techniques which have been developed so far can be applied to the double layer if we regard the surface as a large ion whose diameter is $D \gg \sigma$ and whose charge is Q. Eventually, we take the limit $D \to \infty$. It is convenient to use the charge density on the electrode (or equivalently, the electric field at the electrode, E, which is equal to 4π times the charge density) as a variable. Thus,

$$Q = \frac{ED^2}{4} . \tag{8.1}$$

If $\rho_i(x)$ is the (number) density profile of ions of species i at a distance x from the electrode, then the singlet distribution function or reduced density profile, is

$$\begin{aligned} g_i(x) &= h_i(x) + 1 \\ &= \rho_i(x)/\rho_i , \end{aligned} \tag{8.2}$$

where $\rho_i = \rho_i(\infty)$ is the bulk (number) density of ions of species i. The distance x is measured from the wall itself so that the distance of closest approach is $\sigma/2$.

The density profile of all the ions is

$$\rho(x) = \sum_i \rho_i(x) = \sum_i \rho_i g_i(x) \tag{8.3}$$

and the charge profile is

$$\begin{aligned} e\sum_i z_i\rho_i(x) &= e\sum_i z_i\rho_i g_i(x) \\ &= e\sum_i z_i\rho_i h_i(x) . \end{aligned} \tag{8.4}$$

Changing from $g_i(x)$ to $h_i(x)$ is justified because of the charge neutrality condition in the bulk

$$\sum_i z_i\rho_i = 0. \tag{8.5}$$

If $-E/4\pi$ is the charge density on the electrode,

$$e\sum_i z_i\rho_i \int_{\sigma/2}^{\infty} g_i(t)dt = E/4\pi . \tag{8.6}$$

Force balance considerations(31) require that

$$kT\sum_i \rho_i(\sigma/2) = p + E^2/8\pi\varepsilon \ , \tag{8.7}$$

where p is the pressure of the bulk fluid (the osmotic pressure of an electrolyte). The first term is the momentum transfer to the wall and the second term is the Maxwell stress. The potential at a distance x from the electrode is given by

$$\phi(x) = \frac{4\pi e}{\varepsilon}\sum_i z_i\rho_i\int_x^\infty (t-x)g_i(t)dt. \tag{8.8}$$

Thus, the potential difference across the interface is

$$\begin{aligned} V &= \phi(0) \\ &= \frac{\sigma E}{2\varepsilon} + \phi(\sigma/2) \ , \end{aligned} \tag{8.9}$$

where (8.6) has been used.

If the solvent is discrete, consists of molecules, then most of the above considerations remain valid. The density profile of the ions is given by Eq. (8.3) and the charge profile is given by (8.4). The density profile the solvent molecules is

$$\rho_d(x) = \rho_d g_d^0(x), \tag{8.10}$$

where

$$g_d^0(x) = \frac{1}{4\pi}\int g_d(x,\Omega)d\Omega \ . \tag{8.11}$$

One projection of $g_d(x,\Omega)$ which is of interest is

$$\Delta h_d(x) = \frac{\sqrt{3}}{4\pi}\int g_d(x,\Omega)\cos\theta d\Omega \ . \tag{8.12}$$

Equation (8.7) is modified slightly to become

$$kT\sum_i \rho_i(\sigma/2) + kT\rho_d(\sigma_d/2) = p + E^2/8\pi \ , \tag{8.13}$$

where the sum is over the ion species and p is the actual bulk pressure of the electrolyte. The potential difference across the interface is given by

$$V = 4\pi e \sum_i z_i \rho_i \int_{\sigma/2}^{\infty} t g_i(t)dt + \frac{4\pi}{\sqrt{3}} \rho_d \mu \int_{\sigma_d/2}^{\infty} \Delta h_d(t)dt \ , \qquad (8.14)$$

where σ_d is the diameter of the solvent molecules.

A. *Gouy-Chapman Theory*

Using the charged hard-sphere/dielectric continuum model of an electrolyte, we can apply the Gouy-Chapman theory, developed by Gouy(32) and Chapman(33), and subsequently Stern(34). Assume that

$$g\ (x) = \begin{cases} 0 & (x < \sigma/2), \\ \exp\{\beta z_i e\phi(x)\} & (x > \sigma/2), \end{cases} \qquad (8.15)$$

where $\phi(x)$ is the electrostatic potential which satisfies Poisson's equation

$$\begin{aligned} \frac{d^2\phi}{dx^2} &= \frac{4\pi e}{\varepsilon} \sum_i z_i \rho_i g_i(x) \\ &= \frac{4\pi e}{\varepsilon} \sum_i z_i \rho_i \exp\{\beta z_i e\phi\} \ . \end{aligned} \qquad (8.16)$$

A first integral is always possible since

$$\frac{d^2\phi}{dx^2} = \frac{1}{2} \frac{d}{d\phi} \left(\frac{d\phi}{dx}\right)^2 . \qquad (8.17)$$

Using the fact that

$$\phi = \frac{d\phi}{dx} = 0 \ , \qquad (8.18)$$

at $x = \infty$, we have

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{8\pi kT}{\varepsilon} \sum_i \rho_i [\exp\{\beta z_i e\phi\} - 1]. \qquad (8.19)$$

Now E is constant in the region $0 < x < \sigma/2$. Thus

$$E = - \left.\frac{d\phi}{dx}\right|_{x=\sigma/2}$$

and, thus, Eq. (8.19) for $x = \ /2$ becomes Eq. (8.7) but with p equal to the perfect gas result, ρkT.

To complete the solution, we must integrate Eq. (8.19). In general, this cannot be done analytically. However, for the special case of binary n:n and 1:2 solutions, analytic results can be outlined. Restricting ourselves to the symmetric n:n case,

$$\beta z e\phi(x)/2 = \ln\{1 + Ae^{-\kappa(x-\sigma/2)}\} - \ln\{1 - A\, e^{-\kappa(X-\sigma/2)}\}\,, \qquad (8.21)$$

where $z = |z_i|$,

$$A = \frac{b/2}{1 + \sqrt{1 + \frac{b^2}{4}}} \qquad (8.22)$$

$$b = \frac{\beta z e E}{\varepsilon\kappa}\,, \qquad (8.23)$$

and κ is given by Eq. (6.5). Also,

$$\sinh\beta z e\phi(\sigma/2) = b/2 \qquad (8.24)$$

so that

$$V = \frac{\sigma E}{2\varepsilon} + \frac{2}{\beta z e}\sinh^{-1} b/2. \qquad (8.25)$$

At contact

$$g_i(\sigma/2) = 1 + \frac{b^2}{2} \pm b\sqrt{1 + \frac{b^2}{4}}\,, \qquad (8.26)$$

which satisfies Eq. (8.7) with p equal to ρkT. The integrals of $h_i(x)$ can also be obtained. The results is

$$\int_{\sigma/2}^{\infty} h_i(t)dt = \frac{2}{\kappa}\left[\sqrt{1 + \frac{b^2}{4}} \pm \frac{b}{2} - 1\right], \qquad (8.27)$$

where the positive sign applies to the counterions, etc. From this result we see that Eq. (8.6) is satisfied.

The Gouy-Chapman theory fails to satisfy the contact value theorem, Eq. (8.7), by the difference between p and ρkT. At low concentrations this difference is small. In any case, as the electrode is charged, the quadratic terms, $E^2/8\pi\varepsilon$, rapidly becomes dominant. As a result, for most situations the Gouy-Chapman theory satisfies the contact value theorem to a very good approximation.

The Gouy-Chapman theory profiles have the approximately correct area, i.e., they satisfy Eq. (8.6), and have almost the correct contact values. As a result, we would expect them to be quite accurate. That this is the case can be seen in Fig. 13, where the $g_i(x)$ are compared with recent computer simulations$^{(35)}$ for $z = 1$. The agreement is less satisfactory when $z = 2^{(36)}$ but is still much better than would be expected given the relatively crude assumptions of the Gouy-Chapman theory.

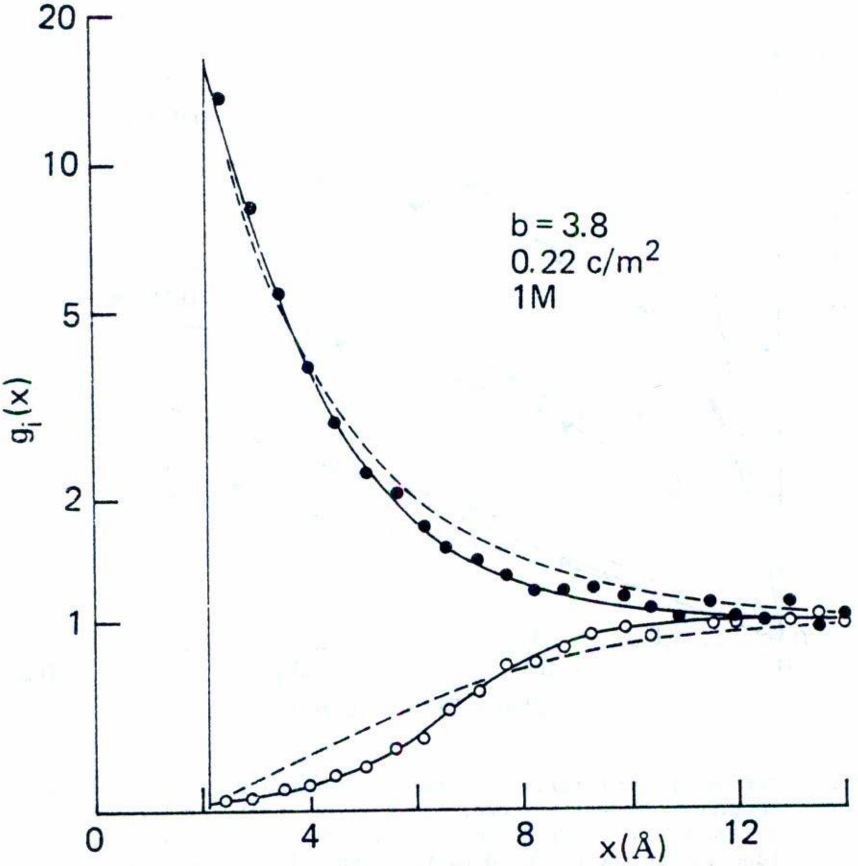

Fig. 13. Singlet distribution functions for the 1M charged hard-sphere/continuum dielectric model electrolyte near a uniformly charged hard wall (charge density = 0.22 coul/m^2) whith $z = 1, \sigma = 4.25$Å, $T = 298$°K, and $\varepsilon = 78.5$. The points give computer simulation results and the broken and solid curves give the GC and HNC/MSA results, respectively.

The Gouy-Chapman values for the diffuse layer potential, $\phi(\sigma/2)$, are compared with computer simulations$^{(35)}$ in Fig. 14 for $z = 1$. The Gouy-Chapman values of $\phi(\sigma/2)$ are significantly in error. The error is even more pronounced for the $z = 2$ case$^{(36)}$. Whether this error can be seen experimentally is problematic since the diffuse layer potentials is small compared to the contributions of the metal and the solvent to the potential. We shall discuss these latter contributions shortly. However, a heuristic theory of these effects can be developed now.

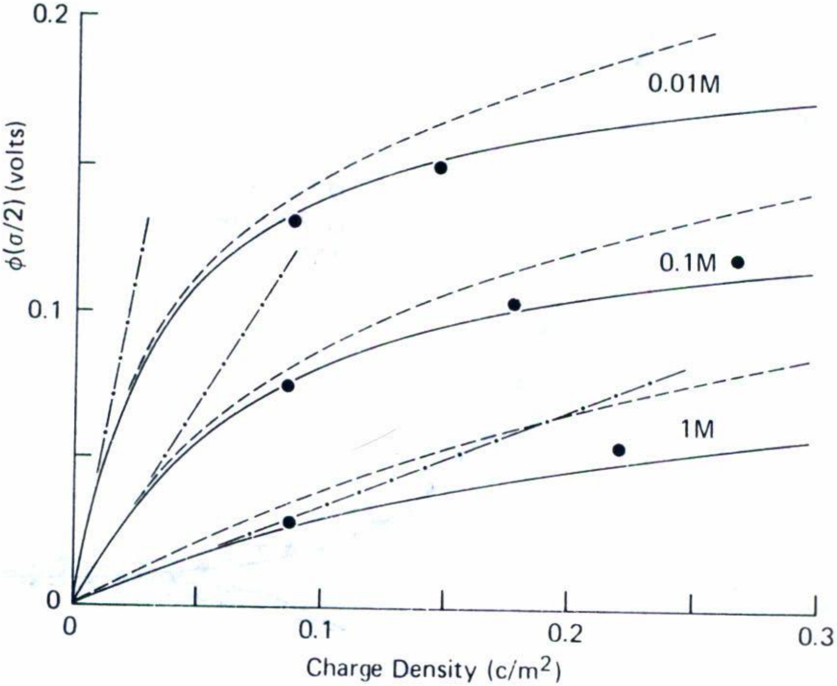

Fig. 14. Diffuse layer potential difference for the charged hard-sphere/continuum dielectric model electrolyte ($z = 1$, $\sigma = 4.25$Å, $T = 298$°K, and $\varepsilon = 78.5$) near a uniformly charged hard wall as a function of the charge density on the electrode. The points give computer simulation results and the curves marked ---, -·-, and —— give the Gouy-Chapman, mean spherical approximation and the HNC/MSA results, respectively.

We see from Eq. (8.25) that V divides itself into two terms, the potential difference across what we can call an "inner layer" where the field is constant and the diffuse layer potential. Let us assume that the effects of the solvent structure and the electronic structure of the metal is such as to modify the effective dielectric constant inside the inner layer but that within the diffuse layer the dielectric constant is equal to the bulk value. If this is the case,

$$V = \frac{\sigma E}{2\varepsilon^*} + \frac{2}{\beta z e} \sinh^{-1} b/2, \qquad 8.28)$$

where ε^* is the effective dielectric constant in the "inner layer".

Thus, the differential capacitance,

$$C_d = \frac{dQ}{dV}, \qquad (8.29)$$

is given by

$$C_d = \frac{\varepsilon}{4\pi} \frac{\kappa\sqrt{1 + \frac{b^2}{4}}}{1 + \frac{\kappa\sigma}{2}\left(\frac{\varepsilon}{\varepsilon^*}\right)\sqrt{1 + \frac{b^2}{4}}} \qquad (8.30)$$

For small charge on the electrode, Eqs. (8.28) and (8.30) become

$$V = \frac{\sigma E}{2\varepsilon^*} + \frac{E}{\varepsilon\kappa} \qquad (8.31)$$

and

$$C_d = \frac{\varepsilon}{4\pi} \frac{\kappa}{1 + \frac{\kappa\sigma}{2}\left(\frac{\varepsilon}{\varepsilon^*}\right)} \qquad (8.32)$$

In Table I we see that Eq. (8.32) with $\varepsilon^* = \varepsilon = 78.4$ is in poor agreement with experiment$^{(37)}$ but is in good agreement if $\varepsilon^* = 4.6$

TABLE I

Differential Capacitante (f/m²) in the Limit of Zero Charge

Conc	Expt(37)	Eq. (8.32) $\varepsilon^* = 78.4$	Eq. (8.32) $\varepsilon^* = 4.6$	Eq. (8.65)	Eq. (8.66)
10^{-4}M		0.0227	0.0211	0.0201	0.0212
10^{-3}M	0.06	0.0710	0.0577	0.0503	0.0579
10^{-2}M	0.13	0.218	0.128	0.0965	0.129
10^{-1}M	0.21	0.630	0.207	0.136	0.210
1M	0.26	1.57	0.257	0.156	0.262

Table I. The experimental results are for an aqueous solution of NaF near a mercury electrode. The theoretical values are calculated with $T = 298°K$, $\varepsilon = 78.4$, and $\sigma = \sigma_d = 2.76$ Å.

Both Eqs. (8.30) and (8.32) have the property that C_d^{-1} consists of two terms, the inverse of the diffuse layer capacitance,

$$C_{dl} = \frac{\varepsilon}{4\pi} \kappa \sqrt{1 + \frac{b^2}{4}} \tag{8.33}$$

or, for small charge

$$C_{dl} = \frac{\varepsilon}{4\pi} \kappa \ , \tag{8.34}$$

which is concentration dependent, and the inverse of a concentration independent term, the "inner layer" capacitance,

$$C_{il} = \frac{\varepsilon}{2\pi\sigma} \ . \tag{8.35}$$

If we differentiate C_d^{-1}, given by Eqs. (8.30) or (8.32), with respect to C_{dl}^{-1}, we obtain

$$\frac{\partial C_d^{-1}}{\partial C_{dl}^{-1}} = 1 \ . \tag{8.36}$$

We see from Fig. 15 that the experimental(38) slope of C_d^{-1} when plotted as a function of C_{dl}^{-1} is indeed unity except at very high concentrations. The good agreement of Eqs. (8.30) and (8.32) with experiment in Fig. 15 and Table I might be thought of as a confirmation of this macroscopic picture

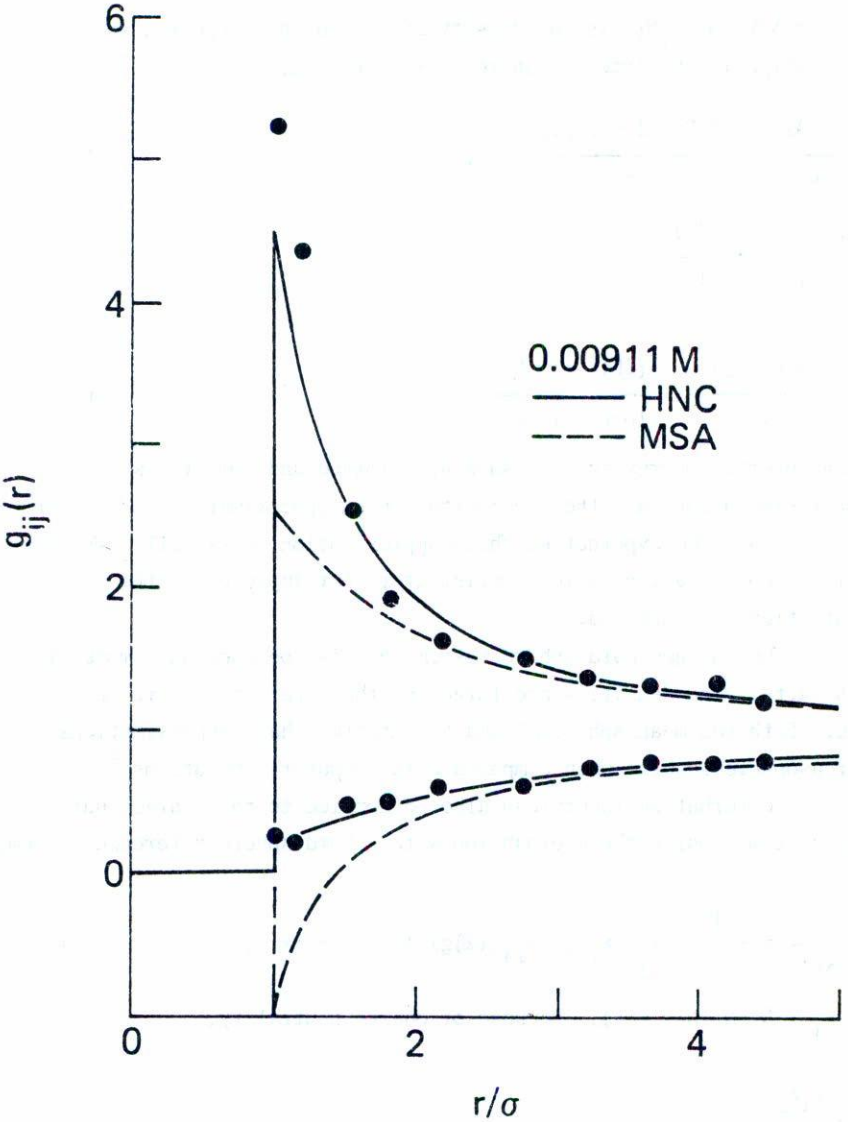

Fig. 5. Radial distribution functions for the charged hard-sphere/continuum dielectric model of a 1:1 electrolyte at 298°K, $\sigma = 4.25$Å, and $\varepsilon = 78.5$. The points give the computer simulation results.

where $\rho = N/V$ $(N = \sum_i N_i)$ is the density of all the hard-spheres and $E_i = E - 3NkT/2$ is the internal energy. From Eq. (6.9)

$$\frac{A - A_0}{NkT} = -\frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} \quad , \tag{6.10}$$

$$\frac{p - p_0}{\rho kT} = -\frac{(2\Gamma)^3}{24\pi\rho} \quad , \tag{6.11}$$

and

$$\beta\frac{\partial(p - p_0)}{\partial\rho} = -\frac{(2\Gamma)^3}{16\pi\rho}\,\frac{1 + \Gamma\sigma}{1 + 2\Gamma\sigma} \quad . \tag{6.12}$$

The MSA internal energy and pressure are plotted and compared with computer simulations and the hypernetted chain approximation results in Figs. 7 and 8. The hypernetted chain approximation works well. The mean spherical approximation is less satisfactory but improves as the concentration is increased.

The charged hard-sphere system can also be used as a model for molten salts. The densities are large and the interactions are very strong. Both the mean spherical and hypernetted chain approximations give reasonable results when compared with computer simulations(10).

Perturbation theory can also be applied to the charged hard sphere system. Using the u-expansion with a hard-sphere reference system,

$$\frac{A - A_0}{NkT} = -\frac{1}{2}\beta\rho\sum_{ij} x_i x_j \int u_{ij}(12)g_0(12)d\mathbf{r}_2 + \cdots \quad , \tag{6.13}$$

where $x_i = N_i/N$ $(N = \sum_i N_i)$. Because of charge neutrality,

$$\sum z_i x_i = 0 \quad , \tag{6.2}$$

the first-order term in Eq. (6.13) vanishes.

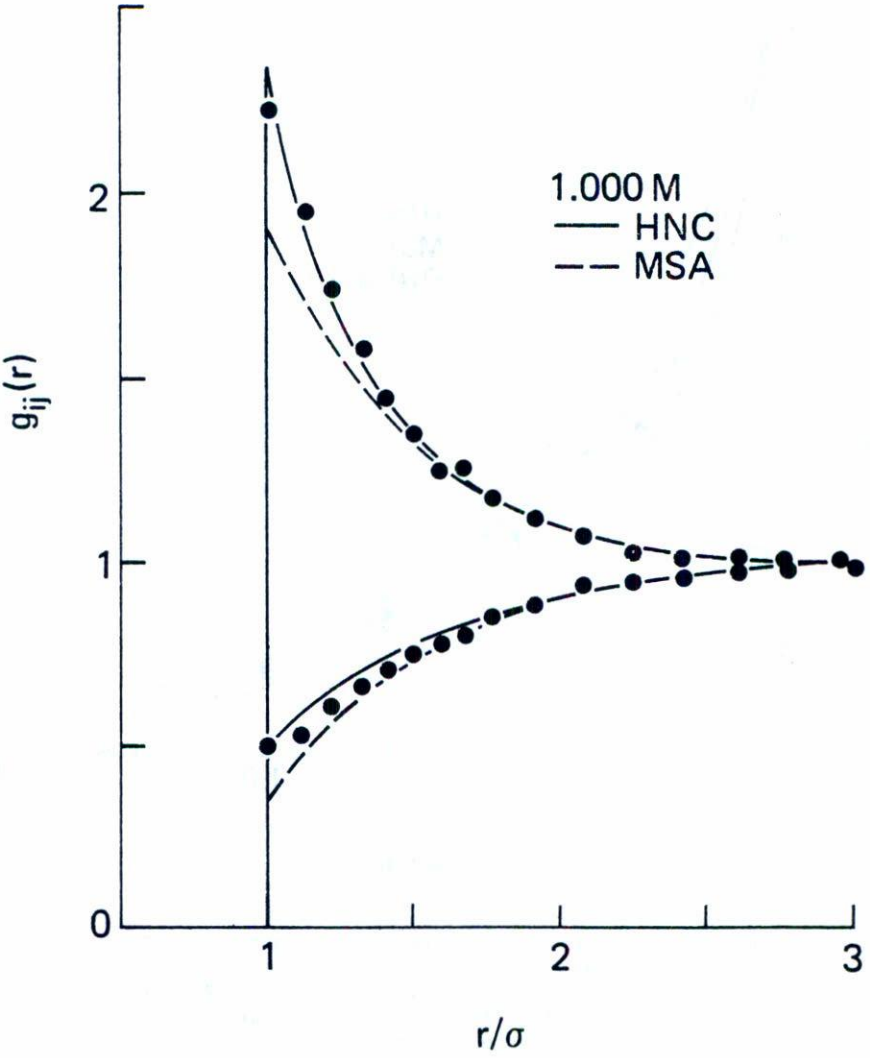

Fig. 6. As in Fig. 5 but with conc = 1.000 M.

In second-order, only the first term in Eq. (4.5) contributes. The other terms vanish because of charge neutrality. Likewise in third-order only the ring diagram is nonzero. Thus,

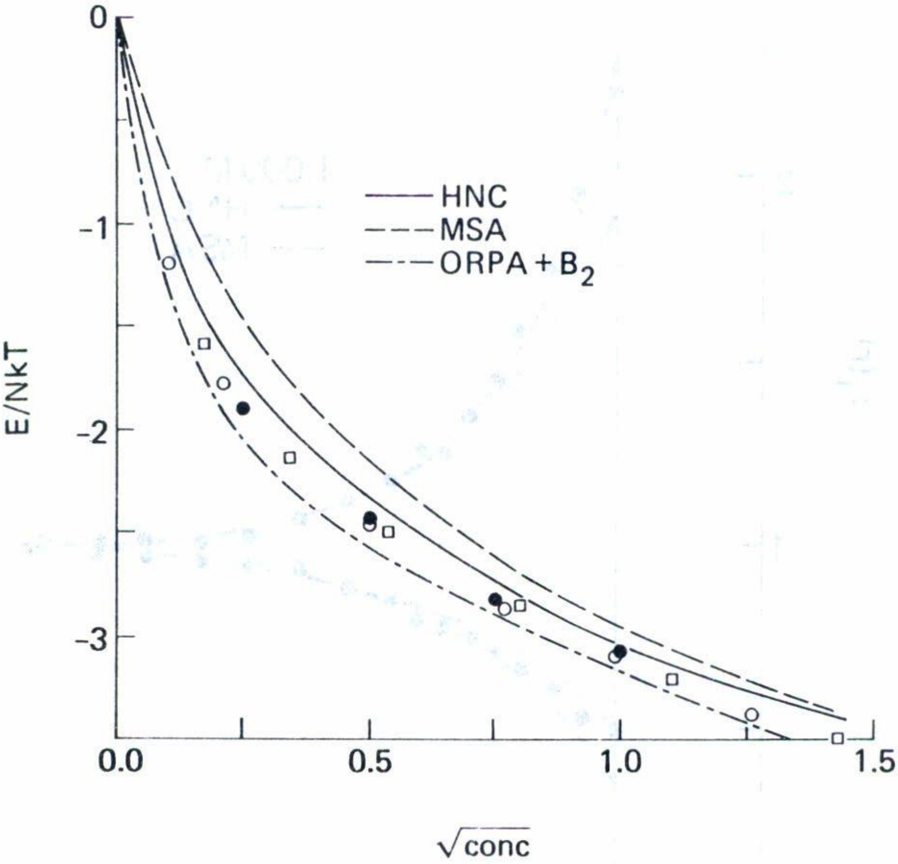

Fig.7. Values of the internal energy for the charged hard-sphere/ continuum dielectric model of a 2:2 electrolyte at 298°K, $\sigma = 4.25$ Å, and $\varepsilon = 78.5$. The points marked, ○, ●, and □ give simulation results of Valleau and Cohen, Valleau and Card, and van Megen and Snook, respectively.

$$\frac{A - A_0}{NkT} = -\frac{1}{4}\beta^2\rho\sum_{ij} x_i x_j \int u_{ij}^2(12)g_0(12)d\underset{\sim}{r}_2 + \frac{1}{6}\beta^3\rho^2\sum_{ijk} x_i x_j x_k \int u_{ij}(12)u_{ik}(13)u_{jk}(23)g_0(123)d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots . \tag{6.14}$$

We see that the cancellation among integrals which leads to small values of the high-order perturbation terms at high densities in the application of perturbation theory to the lattice gas and to simple fluids is not present in this system. Thus, approximations such as Eqs. (4.18) to (4.20) would not be useful for this system. The perturbation series will converge more slowly. None-the-less, we can make progress.

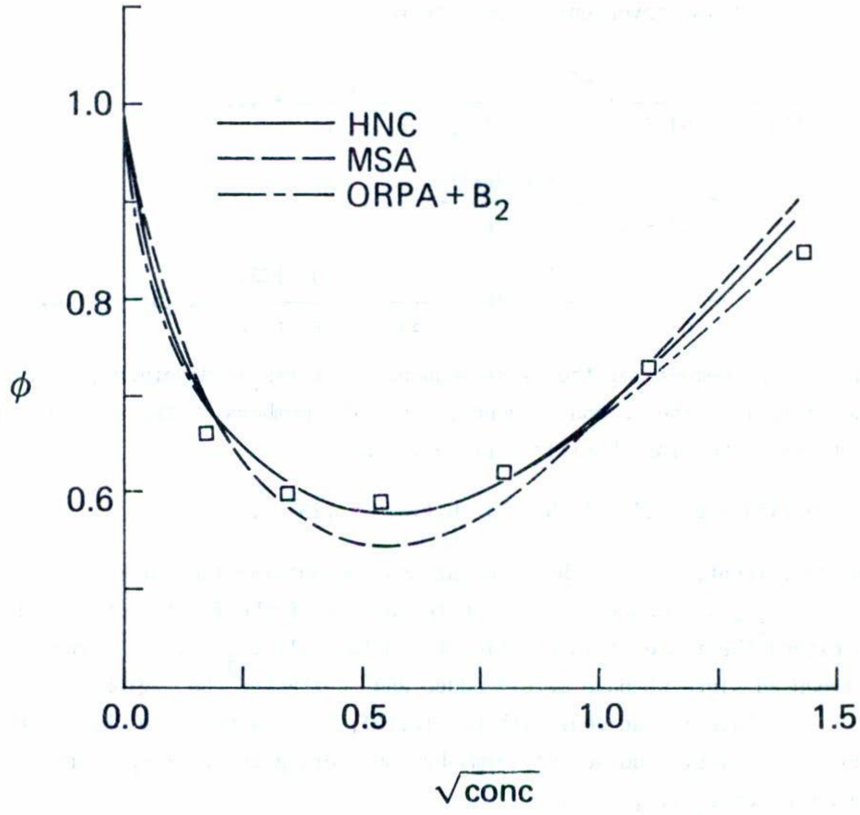

Fig. 8. Values of the osmotic coefficient $\phi = p/\rho kT$ for the charged hard-sphere/continuum dielectric model of a 2:2 electrolyte. The parameters and points are as in Fig. 7.

If we restrict our attention to the symmetric two-component system where $z = |z_1| = |z_2|$, Eq. (6.14) becomes

$$\frac{A - A_0}{NkT} = -\frac{\kappa^4}{64\pi^2\rho}\int \frac{g_0(12)}{r_{12}^2}\,d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int \frac{g_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots . \tag{6.15}$$

Each integral in (6.16) is divergent because of the long range of the Coulomb potential. To get anything useful we must sum these divergent terms.

It is convenient to rewrite Eq. (6.15) as

$$\begin{aligned}\frac{A - A_0}{NkT} = &-\frac{\kappa^4}{64\pi^2\rho}\int \frac{d\underset{\sim}{r}_2}{r_{12}^2} + \frac{\kappa^6}{384\pi^3\rho}\int \frac{d\underset{\sim}{r}_2 d\underset{\sim}{r}_3}{r_{12}r_{13}r_{23}} + \cdots \\ &+ \frac{\kappa^6}{128\pi^3\rho}\int \frac{h_0(12)\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3}{r_{12}r_{13}r_{23}} + \cdots \\ &- \frac{\kappa^4}{64\pi^2\rho}\int \frac{h_0(12)}{r_{12}^2}\,d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int \frac{h_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots .\end{aligned} \tag{6.16}$$

Each of the members of the first sequence of terms is divergent, as is each member of the second sequence. Only the members of the last sequence of terms, involving $h_0(12) = g_0(12) - 1$ and

$$h_0(123) = g_0(123) - 1 - h_0(12) - h_0(13) - h_0(23) \quad , \tag{6.17}$$

are convergent. All of the integrations are outside the cores (i.e., $r_{ij} \geq \sigma$). However, to evaluate the sum of the first sequence, let us extend the range of integration to include all $r_{ij} \geq 0$. No error is introduced since we have merely added and subtracted the regions $0 \leq r_{ij} \leq \sigma$.

Rather than deal with Eq. (6.16), it is simpler to obtain the sum of the first sequence of terms by considering the corresponding expansion of $g_{ij}(r)$, i.e.,

$$\begin{aligned}g_{ij}(r_{12}) = 1 &- \frac{\beta z_i z_j e^2}{\varepsilon}\left\{\frac{1}{r_{12}} - \frac{\kappa^2}{4\pi}\int \frac{d\underset{\sim}{r}_3}{r_{13}r_{23}} + \cdots\right\} \\ &+ \frac{\beta^2 z_i^2 z_j^2 e^4}{2\varepsilon^2 r_{12}^2} + \cdots + \frac{\beta z_i z_j e^2}{\varepsilon} h_0(r_{12}) \frac{\kappa^2}{4\pi}\int \frac{d\underset{\sim}{r}_3}{r_{13}r_{23}} \\ &+ \frac{2\beta z_i z_j e^2}{\varepsilon}\frac{\kappa^2}{4\pi}\int \frac{h_0(13)}{r_{13}r_{23}}\,d\underset{\sim}{r}_3 + \cdots + h_0(r_{12}) - \frac{\beta z_i z_j e^2}{\varepsilon r_{12}} h_0(12)\end{aligned}$$

$$+\frac{\beta z_i^2 z_j^2 e^4}{2\varepsilon^2 r_{12}^2}\, h_0(12) + \dots + \frac{\beta z_i z_j e^2}{\varepsilon}\,\frac{\kappa^2}{4\pi}\int \frac{h_0(123)}{r_{13} r_{23}}\, d\underset{\sim}{r}_3$$

$$+ \dots \quad . \tag{6.18}$$

Again we can assume without loss of generality that Eq. (6.18) is valid for all $r_{ij} \leq 0$. The sequence of terms in the curly brackets is called a ring or chain sum since their terms in this sequence are simple ring diagrams consisting of repeated convolutions of $1/r_{ij}$.

Thus, defining the ring or chain sum,

$$C_{ij}(r_{12}) = \frac{\beta z_i z_j e^2}{\varepsilon} \left\{ \frac{1}{r_{12}} - \frac{\kappa^2}{4\pi} \int \frac{d\underset{\sim}{r}_3}{r_{13} r_{23}} + \dots \right\} , \tag{6.19}$$

and taking the Fourier transform,

$$\hat{C}_{ij}(k) = \frac{4\pi}{k} \int_0^\infty r C_{ij}(r) \sin kr dr, \tag{6.20}$$

we have

$$\hat{C}_{ij}(k) = \frac{4\pi\beta z_i z_j e^2}{\varepsilon k^2} \left\{ 1 - \frac{\kappa^2}{k^2} + \frac{\kappa^4}{k^4} + \dots \right\}$$

$$= \frac{4\pi\beta z_i z_j}{\varepsilon}\, \frac{1}{k^2 + \kappa^2} \, . \tag{6.21}$$

Hence,

$$C_{ij}(r) = \frac{\beta z_i z_j e^2}{\varepsilon}\, \frac{e^{-\kappa r}}{r} \qquad (r \geq 0) \, . \tag{6.22}$$

Keeping only the first two terms in Eq. (6.18) we have the Debye-Hückel approximation

$$g_{ij}(r) = 1 - C_{ij}(r) \, . \tag{6.23}$$

Equation (6.23) is identical to Eq. (6.8). From Eq. (6.23) we obtain

$$E_i/NkT = -\frac{\kappa^3}{8\pi\rho} \quad . \tag{6.24}$$

Hence,

$$\frac{A - A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} \quad . \tag{6.25}$$

Thus, Eq. (6.16) becomes

$$\frac{A - A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{64\pi^2\rho}\int\frac{h_0(12)}{r_{12}^2}\,d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int\frac{h_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \frac{\kappa^6}{128\pi^3\rho}\int\frac{h_0(12)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots \quad . \tag{6.26}$$

Note that as a result of the resummation, the free energy is not an analytic function of β and ρ but is an analytic function of $\beta^{\frac{1}{2}}$ and $\rho^{\frac{1}{2}}$. We must still resum the last sequence (which contains divergent terms). We do this by techniques similar to those used to obtain Eq. (6.22). The result is

$$\frac{A - A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{64\pi^2\rho}\int\frac{h_0(12)}{r_{12}^2}\,e^{-2\kappa r_{12}}\,d\underset{\sim}{r}_2 + \frac{\kappa^6}{384\pi^3\rho}\int\frac{h_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3 + \cdots , \tag{6.27}$$

which may be expanded into the Stell-Lebowitz$^{(11)}$ series

$$\frac{A - A_0}{NkT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{64\pi^2\rho}\int\frac{h_0(12)}{r_{12}^2}\,d\underset{\sim}{r}_2 + \frac{\kappa^5}{32\pi^2\rho}\int\frac{h_0(12)}{r}\,d\underset{\sim}{r}_2 - \frac{\kappa^6}{32\pi^2\rho}\left\langle\left(\int h_0(12)\,d\underset{\sim}{r}_2 - \frac{1}{12\pi}\int\frac{h_0(123)}{r_{12}r_{13}r_{23}}\,d\underset{\sim}{r}_2 d\underset{\sim}{r}_3\right]\right. + \cdots . \tag{6.28}$$

This series converges very slowly. The sum of the series may be approximated by a Padé approximant. The results$^{(12)}$ are very similar to the mean spherical approximation results, obtained from Eqs. (6.9) to (6.12).

We have derived the Stell-Lebowitz expansion from perturbation theory. Stell and Lebowitz did not use this method but obtained their series in a more direct manner. Although the method given here is less direct, it does indicate how improvements may be made.

The integrations in Eq. (6.28) are over all space ($r_{ij} \geq 0$). This is natural in the Stell-Lebowitz derivation. However, in our original perturbation expansion, the integrations are over $r_{ij} \geq \sigma$. This suggests that improved results might be obtained by taking the integrals for the regions $0 \leq r_{ij} \leq \sigma$ and combining them with the κ^3 term. Thus

$$\frac{A - A_0}{NkT} = - \frac{\kappa^3}{12\pi\rho} \left[1 - \frac{3}{4}\,\sigma + \frac{3}{4}\,\kappa\sigma - \frac{7}{8}\,\kappa^3\sigma^3 + \cdots\right] + \cdots \quad . \tag{6.29}$$

At first sight $\kappa^3(1 - 3\kappa\sigma/4 + 3\kappa^2\sigma^2/4 - 7\kappa^3\sigma^3/8 + \cdots)$ seems like an unpromising combination; it is, in fact, $(2\Gamma)^3(1 + 3\Gamma\sigma/2)$. Thus

$$\frac{A - A_0}{NkT} = - \frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} - \frac{\kappa^4}{16\pi\rho}\int_0^\infty h_0(r)dr \; + \cdots \; . \tag{6.30}$$

Retaining only the first term gives the mean spherical approximation.

The corresponding result for $g_{ij}(r)$ is

$$g_{ij}(r) = g_0(r) - C^{MSA}_{ij}(r) - \frac{\beta z_i z_j e^2}{\varepsilon r}\, h_0(r) + \cdots \quad (r > \sigma), \tag{6.31}$$

where

$$C^{MSA}_{ij} = \frac{\beta z_i z_j e^2}{\varepsilon(1 + \Gamma\sigma)^2}\;\frac{f(r - \sigma)}{r} \quad . \tag{6.32}$$

Again, truncation of (6.31) after $C^{MSA}_{ij}(r)$ gives the mean spherical approximation. The optimized random phase approximation of Anderson et al.(13) consists of truncation of Eq. (6.31) after $C^{MSA}_{ij}(r)$ and so is equivalent to the mean spherical approximation.

The series of corrections to the mean spherical approximation still converges slowly and must be summed by Padé methods. There must be extensive cancellation among the terms as the Padé results are not much different from the mean spherical approximation results.

Henderson and Blum(14) have suggested changing the expansion parameter from κ to 2Γ. Thus,

$$\frac{A - A_0}{NkT} = - \frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} - \frac{(2\Gamma)^4}{16\pi\rho}\int_\sigma^\infty h_0(r)\, dr + \cdots \quad . \tag{6.33}$$

The higher-order terms in this expansion are given by Henderson and Blum. Since $2\Gamma \leq \kappa$ this series of corrections to the mean spherical approximation is better behaved. In fact, at normal electrolyte concentrations the corrections are negligible.

At low concentrations, the correction terms, given in Eqs. (6.30) and (6.33) are not the most important corrections to the mean spherical approximation result. This is because, there is, in the fourth-order term [see Eq. (4.12)], the contribution

$$\frac{\Delta A}{NkT} = -\frac{1}{48}\beta^4\rho\sum_{ij}x_i x_j\int u_{ij}^4(r)g_0(r)d\underset{\sim}{r}\ . \tag{6.34}$$

Contributions analogous to this appear in every even-order perturbation term. The corresponding terms in the odd-order perturbation terms do not contribute because of charge neutrality.

The integral in Eq. (6.34) converges because r^{-4} goes to zero sufficiently fast to prevent a divergence. However, since the mean spherical approximation works well at higher densities, the contribution of this β^4 term must disappear at these higher densities due to some cancellation with terms which are higher-order in the density. Hence, even though a resummation is not forced upon us to prevent a divergence, a resummation is desirable as it approximates this cancellation. The effect of the resummation is to replace

$$\beta u_1(r) = \frac{\beta z_i z_j e^2}{\varepsilon r} \tag{6.35}$$

by $C_{ij}(r)$. Thus, we have led to the approximate correction term

$$\frac{\Delta A}{NkT} = -\frac{1}{2}\rho\sum_{ij}x_i x_j\int\sum_{n=2}^{\infty}\left\{\frac{1}{(2n)!}[C_{ij}^{MSA}(12)]^{2n}g_0(12)d\underset{\sim}{r}_2\right\}. \tag{6.36}$$

We could add ΔA given by (6.36) to (6.30) or (6.33) with all the known terms, that is, the integrals (6.28) with the integration region $r_{ij} \geq \sigma$. Andersen et al.(13) keep only the κ^4 term in (6.30) and replace $\beta^2 u_1^2(r)$ in this term by $C_{ij}^2(r)$ to obtain what they call the ORPA+B_2 approximation. In this approximation

$$\begin{aligned}\frac{A - A_0}{NkT} = &-\frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho}\\ &-\frac{1}{4}\rho\sum_{ij}x_i x_j\int h_0(12)[C_{ij}^{MSA}(12)]^2 d\underset{\sim}{r}_2\\ &-\frac{1}{2}\rho\sum_{ij}x_i x_j\int g_0(12)\sum_{n=2}^{\infty}\frac{1}{(2n)!}[C_{ij}^{MSA}(12)]^{2n}d\underset{\sim}{r}_2,\end{aligned} \tag{6.37}$$

which becomes

$$\frac{A - A_0}{NkT} = - \frac{(2\Gamma)^3(1 + 3\Gamma\sigma/2)}{12\pi\rho} - \frac{(2\Gamma)^4}{64\pi^2\rho}\int \frac{h_0(r)}{r^2} f^2(r - \sigma)d\underset{\sim}{r}$$

$$- \frac{1}{2}\rho\sum_{n=2}^{\infty}\frac{1}{(2n)!}\left[\frac{\beta z^2 e^2}{\varepsilon(1 + \Gamma\sigma)^2}\right]^{2n}\int \frac{g_0(r)}{r^{2n}} f^{2n}(r - \sigma)d\underset{\sim}{r} , \qquad (6.38)$$

where the integrations are over the region $r \geq \sigma$. The results of this approximation are shown in Figs. 7 and 8. They are an improvement over the mean spherical approximation results and are comparable to those of the hypernetted chain approximation.

In addition to the theories of electrolytes outlined above, there is another theory of electrolytes which as been useful. It is the modified Poisson-Boltzmann approximation. We do not have time or space to outline this approach here. We have limited ourselves to theories based upon either the Ornstein-Zernike equation or perturbation theory. The modified Poisson-Boltzmann approximation and other approximations have been admirably reviewed by Outhwaite(15).

The theories outlined above provide reasonably good descriptions of the model ionic fluid defined by Eq. (6.1). The main deficiency is the nonmolecular model of the solvent which appears only through the dielectric constant ε. What is needed is a more realistic treatment of the solvent.

7. APPLICATION TO MOLECULAR FLUIDS

Molecular fluids, in which the intermolecular potential depends on orientation as well as position, can be treated by fairly straightforward extensions of the methods discussed above.

First let us consider integral equation approaches. It is sometimes helpful to expand the pair-potential and the correlation functions using an orthogonal basis set. Restricting ourselves for simplicity to molecules with cylindrical symmetry, we have

$$u(1,2) = u^{000}(r) + u^{110}(r)\phi^{110} + u^{112}(r)\phi^{112} + \cdots, \qquad (7.1)$$

etc., where the coefficients are obtained as projections,

$$u^{mnl}(r) = \frac{\int u(1,2)\phi^{mnl}(\Omega_1,\Omega_2)d\Omega_1 d\Omega_2}{\int [\phi^{mnl}(\Omega_1,\Omega_2)]^2 d\Omega_1 d\Omega_2} \quad . \tag{7.2}$$

The first two ϕ^{mnl} (after $\phi^{000} = 1$) are

$$\phi^{110} = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \quad , \tag{7.3}$$

$$\phi^{112} = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \quad , \tag{7.4}$$

where θ_i, ϕ_i are the polar angles of molecule i.

Coupling some approximation with the Ornstein-Zernike equation, Eq. (3.11), gives an approximate integral equation. The simplest is the mean spherical approximation, where

$$c(1,2) = -\beta u(1,2), \tag{7.5}$$

outside the hard core, and

$$h(1,2) = -1 \quad , \tag{7.6}$$

inside the hard core. Because of the linear relation between c(1,2) and u(1,2) in Eq. (7.5) a truncated series for u(1,2) with a limited number of $u^{mnl}(r)$ will produce a similarly truncated series for c(1,2) and h(1,2).

A nonlinear approximation, such as the hypernetted chain approximation, would produce an infinite series for h(1,2) and c(1,2) even if the series for u(1,2) contained a small number of terms. An approximation, based upon the hypernetted chain approximation, which does limit the number of terms in the h(1,2) and c(1,2) expansions is obtained by truncating the expansion of the logarithm in the hypernetted chain approximation,

$$\ln g(1,2) + \beta u(1,2) = h(1,2) - c(1,2) \quad , \tag{7.7}$$

to first order. Thus,

$$c^{000}(r) = h^{000}(r) - \ln\,[1 + h^{000}(r)] - \beta u^{000}(r) \tag{7.8}$$

and

$$c^{mnl}(r) = \frac{h^{000}(r)}{1 + h^{000}(r)} h^{mnl}(r) - \beta u^{mnl}(r), \tag{7.9}$$

for m, n, l not all equal to zero. Equations (7.8) and (7.9) are called the linearized hypernetted chain approximation$^{(16)}$. Although this is a linearized version of the hypernetted chain approximation, it is different from the mean spherical approximation. The linearized hypernetted approximation reduces to the mean spherical approximation if

$$h^{000}(r) \cong 1. \tag{7.10}$$

Gaylor et al.$^{(197)}$ have proposed an alternative linearized hypernetted chain approximation which is an improvement at low densities, at least. An improved approximation, called the quadratic hypernetted chain approximation follows if the logarithm in Eq. (7.7) is expanded to second order.

Other integral equations can be formulated. Cummings et al.$^{(18)}$ have considered some of these and obtained numerical results for short-ranged anisotropic potentials. Here we will limit ourselves to the relative simple dipolar hard-sphere potential,

$$u(1,2) = u_{HS}(r) - \frac{\mu^2}{r_{12}^3} D(1,2), \tag{2.30}$$

where μ is the dipole moment of a molecule and

$$D(1,2) = \phi^{112} \tag{7.11}$$

is given by (2.31) or (7.4), and the mean spherical and linearized hypernetted chain approximations. The dipolar hard-sphere potential is simple not only because of the limited basis set but also because the potential core is spherical.

Wertheim$^{(19)}$ has obtained an analytic solution for the dipolar hard-sphere potential using the mean spherical approximation. Following his notation, he finds

$$h(1,2) = h_s(r_{12}) + h_D(r_{12})D(1,2) + h_\Delta(r_{12})\Delta(1,2), \tag{7.12}$$

where

$$h_s(r) = h^{000}(r), \tag{7.13}$$

$$h_D(r) = h^{112}(r), \tag{7.14}$$

$$h_\Delta(r) = h^{110}(r), \tag{7.15}$$

D(1,2) is given by Eq. (7.11), and

$$\begin{aligned}\Delta(1,2) &= \hat{\mu}_1 \cdot \hat{\mu}_2 \\ &= \phi^{110}.\end{aligned} \tag{7.16}$$

We note that

$$\int D(1,2)d\Omega_1 d\Omega_2 = \int \Delta(1,2)d\Omega_1 d\Omega_i = 0, \tag{7.17}$$

$$\int D^2(1,2)d\Omega_1 d\Omega_2 = \frac{2}{3}, \tag{7.18}$$

$$\int \Delta^2(1,2)d\Omega_1 d\Omega_2 = \frac{1}{3}, \tag{7.19}$$

and that D(1,2) and $\Delta(1,2)$ are orthogonal, i.e.,

$$\int D(1,2)\Delta(1,2)d\Omega_1 d\Omega_2 = 0 \tag{7.20}$$

Wertheim found that $h_s(r)$ is just the Percus-Yevick/mean spherical approximation result for hard-spheres which can be obtained from Eq. (3.28). Further, he found that if κ is defined by

$$\xi = \kappa\eta, \tag{7.21}$$

where $\eta = \pi^2\rho\sigma^3/6$ and ξ is obtained from

$$\begin{aligned}y &= \frac{4\pi\beta\mu^2\rho}{9} \\ &= \frac{1}{3}\,[q(2\xi) - q(-\xi)],\end{aligned} \tag{7.22}$$

where

$$q(x) = \frac{(1+2x)^2}{(1-x)^4}, \tag{7.23}$$

then

$$h_\Delta(r) = \begin{cases} 0 & (r < \sigma), \\ 2\kappa[h_s(r,2\kappa\rho) - h_s(r, -k\rho)] & (r > \sigma), \end{cases} \tag{7.24}$$

and

$$h_D(r) = \begin{cases} 0 & (r < \sigma), \\ \hat{h}_D(r) - \frac{3}{r^3}\int_0^r \hat{h}_D(s)s^2 ds & (r > \sigma), \end{cases} \tag{7.25}$$

where

$$\hat{h}_D(r) = \kappa[2h_s(r,2\kappa\rho) + h_s(r, -\kappa\rho)]. \tag{7.26}$$

The apparently mysterious equations for κ can also be written as

$$\kappa = \int_\sigma^\infty \frac{h_D(r)}{r}\, dr. \tag{7.27}$$

The thermodynamic functions can be calculated from

$$\frac{p}{\rho kT} = 1 + 4\eta y_s(\sigma) - \frac{1}{3}\beta\rho\mu^2 \int \frac{h_D(r)}{r^3}\, d\underset{\sim}{r} \quad , \tag{7.28}$$

$$kT\frac{\partial\rho}{\partial p} = 1 + \rho\int h_s(r) d\underset{\sim}{r} \ , \tag{7.29}$$

or

$$E_i = -\frac{1}{3} N\rho\mu^2 \int \frac{h_D(r)}{r^3}\, d\underset{\sim}{r} \ . \tag{7.30}$$

Equation (7.30) gives by far the most reliable results.

The dielectric constant ε is calculated from

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = y g_k \ , \tag{7.31}$$

where

$$y = \frac{4\pi}{9}\beta\rho\mu^2 \tag{7.32}$$

and

$$g_k = 1 + \frac{1}{3}\rho\int h_\Delta(r)\, d\underset{\sim}{r} \ . \tag{7.33}$$

It is interesting to note that Onsager's approximation for ε is obtained from Eq. (7.31) by putting $g_k = 1$. In the mean spherical approximation

$$\varepsilon = \frac{(1+4\xi)^2(1+\xi)^4}{(1-2\xi)^6} . \tag{7.34}$$

The mean spherical approximation pair distribution function for dipolar hard-spheres is compared with computer simulation results(20,21) shown in Fig. 9. The mean spherical approximation gives fairly good results for $h_s(r)$. Furhter we see that the simulation $h_s(r)$ for dipolar hard-spheres is very nearly equal to that for hard spheres but is somewhat larger. The mean spherical approximation for $h_D(r)$ and $h_\Delta(r)$ are rather poor. Interestingly, the approximations

$$h_D(r) = g_s(r)h_D^{MSA}(r) \tag{7.35}$$

$$h_\Delta(r) = g_s(r)h_\Delta^{MSA}(r) \tag{7.36}$$

are much better.

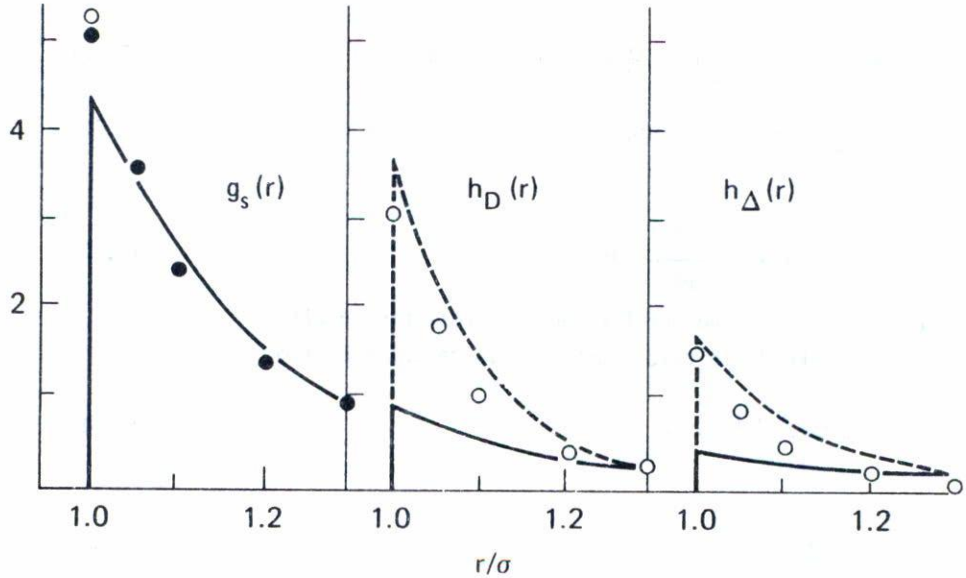

Fig. 9. Pair distribution functions for the dipolar hard-sphere fluid at $\rho\sigma^3 = 0.9$. The points given by ● and ○ give the computer simulation results for $\beta\mu^2 = 0$ (hard-spheres) and $\beta\mu^2 = 1$, respectively. The solid and broken curves give the results of the MSA and Eqs. (7.35) and (7.36), respectively, for $\beta\mu^2 = 1$.

arose naturally and simply. The difficulty with perturbation theory is that it is unclear how to proceed beyond the simple linear approximation in Eq. (8.96). The B_2 approximation is one possibility. Unfortunately, we do not have a theory analogous to the Gouy-Chapman theory to guide us as was the case with Eq. (8.86). However, something analogous to Eq. (8.86) may have some promise.

REFERENCES

1. J.A. Barker, in Rare Gas Solids (M.L. Klein and J.A. Venables, Eds.), Academic Press, New York, 1976, Vol. 1, Chap. 4.
2. H. Eyring, D. Henderson, B.J. Stover, and E.M. Eyring, Statistical Mechanics and Dynamics, 2nd Ed., Wiley-Interscience, New York, 1982.
3. J.A. Barker and D. Henderson, Rev. Mod. Phys. 48 (1976) 587.
4. E.Waisman and J.L. Lebowitz, J. Chem. Phys. 52 (1970) 4307; 56 (1972) 3086,3093.
5. L. Blum, Mol. Phys. 30 (1975) 2529.
6. D. Henderson and W.R. Smith, J. Stat. Phys. 19 (1978) 191.
7. J.C. Rasaiah and H.L. Friedman, J. Chem. Phys. 48 (1968) 2742.
8. D.N. Card and J.P. Valleau, J. Chem. Phys. 52 (1970) 6232; J.P. Valleau and L.K. Cohen, J. Chem. Phys. 72 (1980) 5935; J.P. Valleau, L.K. Cohen, and D. Card, J. Chem. Phys. 72 (1980) 5942.
9. W. van Megen and I.K. Snook, Mol. Phys. 39 (1980) 1043.
10. B. Larsen, Chem. Phys. Letters 27 (1974) 47.
11. G. Stell and J.L. Lebowitz, J. Chem. Phys. 49 (1968) 3796
12. B. Larsen, J.C. Raisiah, and G. Stell, Mol. Phys. 33 (1977) 987.
13. H.C. Andersen and D. Chandler, J. Chem. Phys. 53 (1970) 547; H.C. Andersen, D. Chandler, and J.D. Weeks, J. Chem. Phys. 56 (1972) 3812; H.C. Andersen and D. Chandler, J. Chem. Phys. 57 (1972) 1918; H.C. Andersen, D. Chandler, and J.D. Weeks, Adv. Chem. Phys. 34 (1976) 105.
14. D. Henderson and L. Blum, Mol. Phys. 40 (1980) 1509.
15. C.W. Outhwaite, in Statistical Mechanics (Specialist Periodical Reports), K. Singer, Ed., Chemical Society, London, 1975, Vol. 2, Chap. 3.
16. G.N. Patey, Mol. Phys. 34 (1977) 427; 35 (1978) 1413.
17. K.J. Gaylor, D.J. Isbister, and R.O. Watts, Mol. Phys. 47 (1982) 55.
18. P.T. Cummings, J. Ram, R. Barker, C.G. Gray, and M.S. Wertheim, Mol. Phys. 48 (1983) 1177.
19. M.S. Wertheim, J. Chem. Phys. 55 (1971) 4291.
20. J.A. Barker and D. Henderson, Mol. Phys. 21 (1971) 187; Ann. Rev. Phys. Chem. 23 (1972) 439.
21. L. Verlet and J.J. Weis, Mol. Phys. 28 (1974) 665.
22. J.A. Barker, D. Henderson, and W.R. Smith, Mol. Phys. 17 (1969) 579.
23. A. Tani, D. Henderson, J.A. Barker, and C.E. Hecht, Mol. Phys. 48 (1983) 863.
24. G.S. Rushbrooke, G. Stell, and H.S. Høye, Mol. Phys. 26 (1973) 1199.
25. G.N. Patey and J.P. Valleau, Chem. Phys. Letters 21 (1973) 297; J. Chem. Phys. 64 (1976) 170.

26. D.Levesque, G.N. Patey, and J.J. Weis, Mol. Phys. 34 (1977) 1077; S. DeLeeuw, J.W. Perram, and E.R. Smith, Proc. Roy. Soc. A373, (1980) 27; D.J. Adams, Mol. Phys. 40 (1980) 1261.
27. W.R. Smith, W.G. Madden, and D.D. Fitts, Chem. Phys. Letters 36, (1975) 195.
28. L. Blum, Chem. Phys. Letters 26 (1974) 200; J. Chem. Phys. 61 (1974) 2129; J. Stat. Phys. 18 (1978) 451; F. Vericat and L. Blum, J. Stat. Phys. 22 (1980) 593; Mol. Phys. 45 (1982) 1067.
29. D. Henderson and L. Blum, unpublished work.
30. C.G. Gray and K.E. Gubbins, Theory of Molecular Fluids, Oxford University Press, Oxford (in press).
31. D. Henderson, L. Blum, and J.L. Lebowitz, J. Electroanal. Chem. 102 (1979) 315.
32. G. Gouy, J. Phys. 9 (1910) 457.
33. D.L. Chapman, Phil Mag. 25 (1913) 475.
34. O. Stern, Z. Elektrochem. 30 (1924) 508.
35. G.M. Torrie and J.P. Valleau, J. Chem. Phys. 73 (1980) 5807.
36. G.M. Torrie and J.P. Valleau, J. Phys. Chem. 86 (1982) 325.
37. D.C. Grahame, unpublished results quoted by R. Parsons, in Modern Aspects of Electrochemistry, J. O'M. Bockris, Ed., Buttersworth, London, 1954, Vol. 1, p. 148.
38. R. Parsons and F.G.R. Zobel, J. Electroanal. Chem. 9 (1965) 333.
39. D. Henderson, J. Barojas, and M. Lozada-Cassou, J. Phys. Chem. (in press).
40. D. Henderson, J. Barojas, and L. Blum, J. Phys. Chem. (in press).
41. D. Henderson, L. Blum, and W.R. Smith, Chem. Phys. Letters 63 (1979) 381; D. Henderson and L. Blum, J. Electroanal. Chem 11 (1980) 217; M. Lozada-Cassou, R. Saavedra-Barrera, and D. Henderson, J. Chem. Phys. 77 (1982) 5150; M. Lozada-Cassou and D. Henderson, J. Phys. Chem. (in press).
42. S.L. Carnie, D.Y.C. Chan, D.J. MItchell, and B. Ninham, J. Chem. Phys. 74 (1981) 1472.
43. C.W. Outhwaite, J. Chem. Soc. Faraday II 74 (1978) 1214; S. Levine and C.W. Outhwaite, J. Chem. Soc. Faraday II 74 (1978) 1670; C.W. Outhwaite, L.B. Bhuiyan, and S. Levine, Chem. Phys. Letters 64 (1979) 150; L.B. Bhuiyan, C.W. Outhwaite, and S. Levine, Chem. Phys. Letters 66 (1979) 321; C.W. Outhwaite, L.B. Bhuiyan, and S. Levine, J. Chem. Soc. 76 (1980) 1388; S. Levine, C.W. Outhwaite, and L.B. Bhuiyan, J. Electroanal. Chem. 123 (1981) 105; C.W. Outhwaite, L.B. Bhuiyan, and S. Levine, Chem. Phys. Letters 78 (1981) 413; L.B. Bhuiyan, C.W. Outhwaite, and S. Levine, Mol. Phys. 42 (1981) 1271; C.W. Outhwaite, and L.B. Bhuiyan, J. Chem. Soc. Faraday II 78 (1982) 775; 79 (1983) 707.
44. S.L. Carnie and G.M. Torrie, Adv. Chem. Phys. (in press).
45. L. Blum, J. Phys. Chem. 81 (1977) 136.
46. S.L. Carnie and D.Y. Chan, J. Chem. Phys. 73 (1980) 2949; L. Blum and D. Henderson, J. Chem. Phys. 74 (1981) 1902; D. Henderson and L. Blum, J. Electroanal. Chem. 132 (1982) 1.
47. J.P. Badiali, M.L. Rosenberg, F. Vericat, and L. Blum, J. Electroanal. Chem. (in press).
48. W. Schmickler and D. Henderson, J. Phys. Chem. (in press).
49. M.L. Rosinberg, Thesis, Université Pierre et Marie Curie, Paris, 1983.
50. L. Blum, D. Henderson, and R. Parsons, J. Electroanal. Chem. (in press).